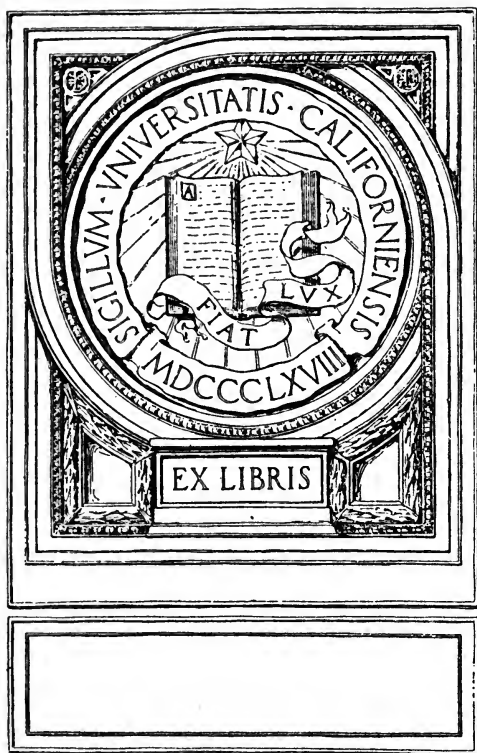
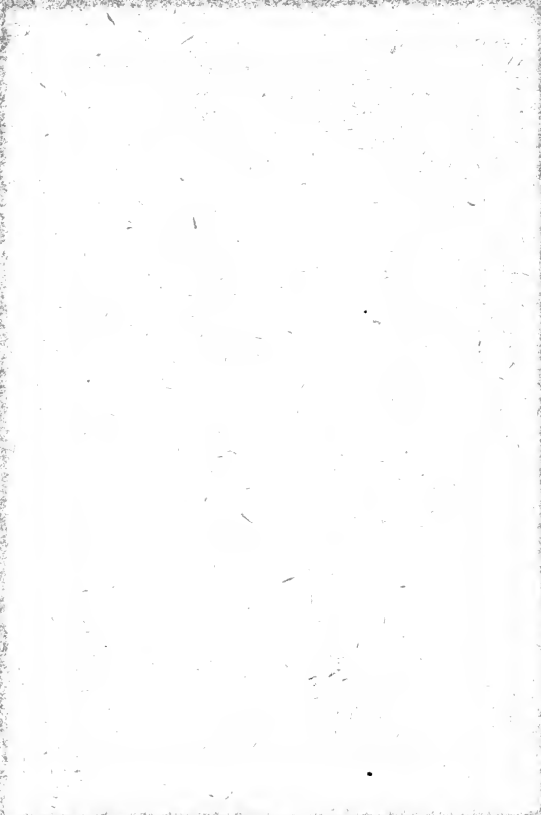
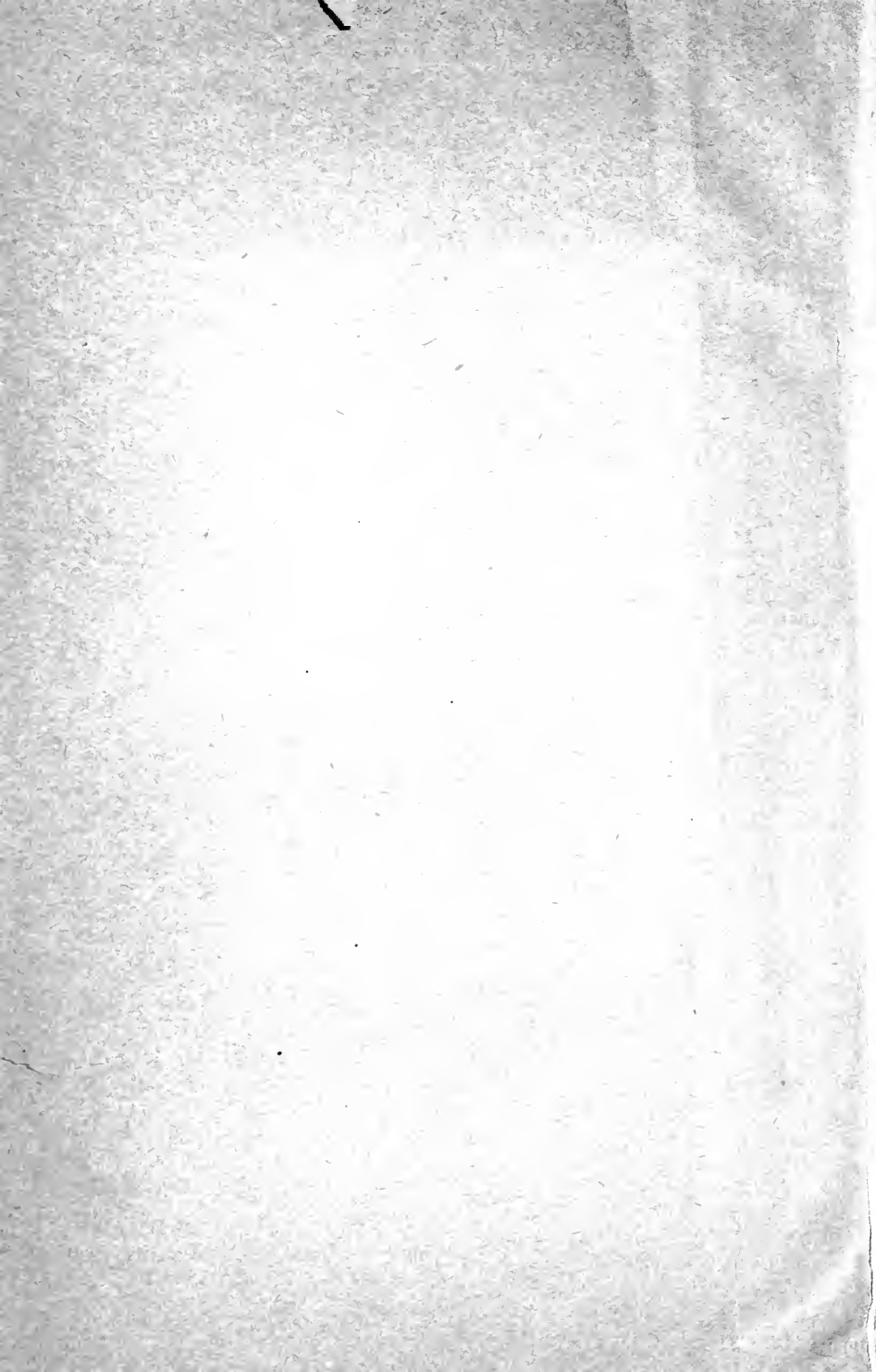


**THE  
BRITISH  
COAL-TAR  
INDUSTRY**

**W.M.GARDNER**













THE BRITISH  
COAL-TAR INDUSTRY



# THE BRITISH COAL-TAR INDUSTRY

ITS ORIGIN, DEVELOPMENT,  
AND DECLINE

EDITED BY

WALTER M. GARDNER, M.Sc., F.I.C.

PRINCIPAL OF THE BRADFORD TECHNICAL COLLEGE; EDITOR OF THE  
"JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS"

WITH ILLUSTRATIONS

PHILADELPHIA  
J. B. LIPPINCOTT COMPANY  
LONDON: WILLIAMS & NORGATE

TP 953  
C13

# CONTENTS

	PAGE
INTRODUCTION . . . . .	vii
I. 1868. THE ANILINE OR COAL-TAR COLOURS. By W. H. PERKIN, F.R.S. (Cantor Lectures) . . . . .	I
II. 1870. THE ARTIFICIAL PRODUCTION OF ALIZARINE. By Professor H. E. ROSCOE, F.R.S. . . . .	46
III. 1879. THE HISTORY OF ALIZARIN AND ALLIED COLOURING MATTERS. By W. H. PERKIN, F.R.S. . . . .	54
IV. 1880. THE NEWER ARTIFICIAL COLOURING MATTERS DERIVED FROM BENZENE. By R. J. FRISWELL, F.C.S., F.I.C. . . . .	60
V. 1881. INDIGO AND ITS ARTIFICIAL PRODUCTION. By Professor H. E. ROSCOE, LL.D., F.R.S. . . . .	71
VI. 1885. THE COLOURING MATTERS PRODUCED FROM COAL-TAR. By W. H. PERKIN, F.R.S. . . . .	75
VII. 1886. RECENT PROGRESS IN THE COAL-TAR INDUSTRY. By Professor Sir H. E. ROSCOE, M.P., LL.D., F.R.S. . . . .	106
VIII. 1886. THE SCIENTIFIC DEVELOPMENT OF THE COAL-TAR COLOUR INDUSTRY. By Professor R. MELDOLA, F.C.S., F.I.C. . . . .	121
IX. 1896. THE ORIGIN OF THE COAL-TAR COLOUR INDUSTRY AND THE CONTRIBUTION OF HOFMANN AND HIS PUPILS. (Hofmann Memorial Lecture.) By W. H. PERKIN, Ph.D., D.C.L., F.R.S. . . . .	141
X. 1901. THE SYNTHESIS OF INDIGO. By Professor R. MELDOLA, F.R.S., F.I.C. . . . .	188
XI. 1901. THE RELATIVE PROGRESS OF THE COAL-TAR INDUSTRY IN ENGLAND AND GERMANY DURING THE PAST FIFTEEN YEARS. By ARTHUR G. GREEN, F.I.C., F.C.S. . . . .	189
XII. 1901. THE INDIGO CRISIS . . . . .	204
XIII. 1902. APPLIED CHEMISTRY, ENGLISH AND FOREIGN. By Sir J. DEWAR, M.A., LL.D., D.Sc., F.R.S. . . . .	222
XIV. 1903. THE RELATION BETWEEN SCIENTIFIC RESEARCH AND CHEMICAL INDUSTRY. By Professor R. MELDOLA, F.R.S. . . . .	227



	PAGE
XV. 1905. HISTORY OF THE COAL-TAR COLOUR INDUSTRY BETWEEN 1870 AND 1885. By Professor R. MELDOLA, F.R.S. . . . .	228
XVI. 1906. NOTE ON THE PERKIN JUBILEE . . . . .	232
XVII. 1908. PERKIN OBITUARY NOTICE. By Professor R. MELDOLA, F.R.S. . . . .	233
XVIII. 1908. THE FOUNDING OF THE COAL-TAR COLOUR INDUSTRY. By Professor R. MELDOLA, F.R.S. . . . .	234
XIX. 1908. LETTER FROM PROFESSOR H. CARO TO PROFESSOR R. MELDOLA, MAY 1908 . . . . .	257
XX. 1910. TINCTORIAL CHEMISTRY, ANCIENT AND MODERN. By Professor R. MELDOLA, F.R.S. . . . .	259
XXI. 1910. PATENT LAW IN RELATION TO THE DYEING INDUSTRY. By A. G. BLOXAM, F.I.C. . . . .	269
XXII. 1910. THE COAL-TAR COLOUR INDUSTRY OF ENGLAND: CAUSES OF ITS PROGRESS AND RETARDATION. By I. SINGER . . . . .	280
XXIII. 1914. THE ARTIFICIAL COLOUR INDUSTRY AND ITS POSI- TION IN THIS COUNTRY. By F. M. PERKIN, Ph.D., F.I.C. . . . .	298
XXIV. 1914. THE SUPPLY OF CHEMICALS TO BRITAIN AND HER DEPENDENCIES. By Sir WILLIAM A. TILDEN, D.Sc., LL.D., F.R.S. . . . .	315
XXV. 1914. BRITAIN AND GERMANY IN RELATION TO THE CHEMICAL TRADE. By WILLIAM R. ORMANDY, D.Sc., F.C.A. . . . .	335
XXVI. 1914. THE MANUFACTURE OF ANILINE DYES IN ENGLAND. By The Right Hon. Lord-Justice MOULTON, P.C., K.C., F.R.S. . . . .	351
XXVII. 1915. GERMAN CHEMICAL INDUSTRY THIRTY YEARS AGO. By The Right Hon. Sir H. ROSCOE, F.R.S. . . . .	365
XXVIII. 1915. THE MANUFACTURE OF DYESTUFFS IN BRITAIN. By Professor W. M. GARDNER, M.Sc., F.I.C. . . . .	371
XXIX. 1915. THE CHEMICAL INDUSTRIES OF GERMANY. By Professor P. FRANKLAND, F.R.S. . . . .	379
XXX. 1915. PATENT LAW REFORM. By J. W. GORDON, K.C. . . . .	389
XXXI. 1915. THE SUPPLY OF DYEWARES. By Professor R. MELDOLA, D.Sc., LL.D., F.R.S. . . . .	401
XXXII. 1915. THE POSITION OF THE ORGANIC CHEMICAL IN- DUSTRY. By Professor W. H. PERKIN, F.R.S. . . . .	407
INDEX OF NAMES . . . . .	429
INDEX OF COLOURING MATTERS . . . . .	434
TABULAR AND STATISTICAL INFORMATION . . . . .	437

## INTRODUCTION

As a side issue of the war the industry of the manufacture of synthetic dyestuffs has been brought prominently before the public during the past twelve months. And this has occurred not because of its magnitude—for the annual value of the products used in Britain did not much exceed £2,000,000,—but because the products were essential to the carrying on of the great textile industries of the country, and they were chiefly imported from Germany.

It was quickly recognised that our virtual dependence upon Germany for dyestuffs jeopardised our textile trade and many others, such as the manufacture of paints, which involve the use of pigments ; and the annual value of the industries concerned cannot be less than £220,000,000. The stock of dyewares held in this country is never equal to more than a few months' supply, and the processes involved in their production are of such a nature that the manufacture cannot quickly be improvised. Realising therefore that the resources of private enterprise were unequal to the task of making the necessary provision, the Government appointed a commission of inquiry which eventually resulted in the formation of a State-aided limited company—British Dyes Ltd.—established to manufacture or otherwise provide synthetic dyestuffs on a scale commensurate with the national requirements.

The history of the origin and development of the coal-tar colour industry is of great interest not only to the chemist and the student of industrial economics, but also to the politician, the leader of industry, and even to the general reader. To each of

these it has a significant message. The industry which originated and received its early development in this country has grown to be one of great profit and importance, but after a period of much prosperity here (1856 to about 1870) it became gradually more and more centralised in Germany, and has latterly been one of her most profitable industries; the average dividend paid by the six largest manufacturing firms being upwards of 20 per cent. on a nominal capital of about £8,000,000, which represents only a small fraction of the capital actually expended, most of which has been written off out of profits.

The development in Germany of many other associated industries has been the direct outcome of the success of their dyestuffs industry; for example, the production of synthetic medicines, scents and flavourings, the manufacture of photographic drugs and of fine chemicals generally, the production of artificial fertilisers and of high explosives, and the incidental production of the necessary reagents—such as sulphuric acid and caustic soda—on an enormous scale.

The ramifications of the influence of the coal-tar colour industry in Germany are indeed most astonishing, and a close investigation of the causes of their success will well repay those who are responsible for the future success of British industry.

It is with the object of affording easily accessible material for such an inquiry that this book has been compiled. It comprises the chief lectures and addresses given in this country on the subject since the establishment of the industry by Perkin in 1856 to the present day. The papers are given in chronological order, and the book naturally divides itself into two portions, the first twenty-two papers (pp. 1 to 297) dealing with the history and development of the industry, and the latter portion (Papers XXIII. to XXXII., pp. 298 to 427) dealing with the problem as it has presented itself since the outbreak of the war.

The reasons given for the relative decline of the British industry and its phenomenal development in Germany are numerous and varied. Amongst the former may be mentioned

the supposed lack of well-trained chemists in this country, our admitted early neglect of chemical research, defects in our patent laws, the excise restrictions on alcohol, our fiscal system, want of enterprise and of co-operation amongst the British manufacturers, apathy of successive Governments towards industry (as distinct from commerce), and the early neglect of science by the old universities which is not unconnected with a corresponding ignorance and neglect on the part of our legislators and the general mass of citizens.

These various topics are all dealt with in one or other of the papers reprinted herein, and they have a direct bearing not only on industries based on organic chemistry—such as those mentioned in a previous paragraph,—but have also a profound bearing on the general question of the relation of science to industry. And it cannot be too often or too strongly stated that the future of British industry depends on a full utilisation of science in our industries.

One point which is frequently lost sight of in discussing the reasons for our virtual loss of the coal-tar colour industry is that this industry has not been largely developed in any country other than Germany. If countries differing so widely in fiscal, excise, and patent laws, governmental and public appreciation of science, industrial conditions, etc., as Britain, France, and the United States, are equally unable to develop a particular industry which flourishes in Germany, this appears to point to the existence of some specially favourable set of conditions in Germany rather than to the action of some deterrent condition in Britain.

The compiler of the book desires to express his great indebtedness to the authors of the various papers, and to the editors of the journals in which they originally appeared, for their kind permission to reproduce them herein.

WALTER M. GARDNER.

BRADFORD, *September 1st*, 1915.



I. : 1868

## THE ANILINE OR COAL-TAR COLOURS

BY W. H. PERKIN, F.R.S.

(Cantor Lectures : *Journal of the Society of Arts*, 1868,  
pp. 99, 109, 121)

### I

#### COAL TAR, BENZOL, NITROBENZOL, ANILINE, AND ANILINE PURPLE OR MAUVE

IN this short course of lectures it is my desire to bring before you a somewhat condensed history of the artificial colouring matters, generally known as the "coal-tar colours." By this designation it is not meant to imply that colouring matters actually exist in coal tar, and may, therefore, be extracted from it, but that coal tar is the source of certain products which, when changed by various chemical processes, are capable of yielding coloured derivatives. You will thus perceive that it is important for us to consider the various means employed to obtain the raw materials before giving our attention to the colouring matters themselves. We will, therefore, at once proceed to the consideration of "coal tar," its formation and constitution.

Coal tar consists of the oily fluid formed by the destructive distillation of coal, and is obtained as a secondary product in the manufacture of coal gas. Originally, coal tar was a great nuisance to the gas manufacturer, and it was often a problem to him what he should do with it. I need scarcely say that this state of things is now changed. In the gasworks the coal is distilled in large retorts, sometimes twenty-five or thirty feet in length. They are made of fireclay or iron, and several are arranged in one furnace, or oven, as it is usually termed. Each retort is fitted with an iron mouthpiece, from which a vertical tube rises, the mouthpiece also having a door fastened with a cross-bar and screw.

When in use these retorts are rapidly filled with coal by means of a proper scoop, and then the doors luted and fixed so as to be airtight. Distillation commences immediately, as the retorts are constantly kept red-hot. The gas and other products which form pass up the front vertical pipe (connected with the mouthpiece), through a bend, and down into a long horizontal tube, called the "hydraulic main." Here most of the oily products condense, and as they accumulate pass on with the gas down the general main and flow into a tank provided for their reception. These oily products constitute "coal tar." The coal gas, leaving this tar behind, passes on to the condensers, and deposits a second but smaller quantity of tar, and is then purified and stored in the gas holders. The gas, however, does not interest us now.

I am here distilling some coal in a small glass retort, the beak of which is inserted into one of the openings of a three-necked receiver. The second opening is connected with a tube, so that the gaseous products may be examined, whilst the third and lower one is fitted to a small bottle, in which you see we have already obtained a quantity of an oily fluid. This is our coal tar.

Having now seen how coal tar is produced, we will consider of what it consists. Coal tar is by no means a definite body, but contains a great number of different substances, as a glance at the following table will show :—

TABLE I.—PRODUCTS OF THE DISTILLATION OF COAL.

Name.	Formula.	Boiling-point Centigr.
Hydrogen . . . . .	HH	...
Marsh gas (hydride of methyl) . . . . .	(CH <sub>3</sub> )H	...
Hydride of hexyl . . . . .	(C <sub>6</sub> H <sub>13</sub> )H	65
Hydride of octyl . . . . .	(C <sub>8</sub> H <sub>17</sub> )H	106
Hydride of decyl . . . . .	(C <sub>10</sub> H <sub>21</sub> )H	158
Olefiant gas (ethylene) . . . . .	C <sub>2</sub> H <sub>4</sub>	...
Propylene (tritylene) . . . . .	C <sub>3</sub> H <sub>6</sub>	...
Caproylene (hexylene) . . . . .	C <sub>6</sub> H <sub>12</sub>	55
Enanthylene (heptylene) . . . . .	C <sub>7</sub> H <sub>14</sub>	99
Paraffin . . . . .	C <sub>n</sub> H <sub>n</sub>	...
Acetylene . . . . .	C <sub>2</sub> H <sub>2</sub>	...
Benzol . . . . .	C <sub>6</sub> H <sub>6</sub>	80·8
Parabenzol . . . . .	C <sub>6</sub> H <sub>6</sub>	97·5
Toluol . . . . .	C <sub>7</sub> H <sub>8</sub>	110
Xylol . . . . .	C <sub>8</sub> H <sub>10</sub>	139



TABLE I.—*continued.*

Name.	Formula.	Boiling-point Centigr.
Cumol . . . . .	$C_9H_{12}$	148·4
Cymol . . . . .	$C_{10}H_{14}$	170·7
Naphthaline . . . . .	$C_{10}H_8$	212
Paranaphthaline (anthracene) . . . . .	$C_{14}H_{10}$	...
Chrysen . . . . .	$C_6H_4$	...
Pyren . . . . .	$C_{15}H_4$	...
Water . . . . .	$\left\{ \begin{smallmatrix} H \\ H \end{smallmatrix} \right\} O$	100
Hydrosulphuric acid . . . . .	$\left\{ \begin{smallmatrix} H \\ H \end{smallmatrix} \right\} S$	...
Hydrosulphocyanic acid . . . . .	$\left\{ \begin{smallmatrix} H \\ (CN) \end{smallmatrix} \right\} S$	...
Carbonic oxide . . . . .	CO	...
Carbonic anhydride . . . . .	CO <sub>2</sub>	...
Bisulphide of carbon . . . . .	CS <sub>2</sub>	47
Sulphurous anhydride . . . . .	SO <sub>2</sub>	- 10
Acetic acid . . . . .	$\left\{ \begin{smallmatrix} H \\ (C_2H_3O) \end{smallmatrix} \right\} O$	120
Carbolic acid (phenol) . . . . .	$\left\{ \begin{smallmatrix} H \\ (C_6H_5) \end{smallmatrix} \right\} O$	188
Cresylic alcohol (cresol) . . . . .	$\left\{ \begin{smallmatrix} H \\ (C_7H_7) \end{smallmatrix} \right\} O$	203
Phlorylic alcohol (phlorol) . . . . .	$\left\{ \begin{smallmatrix} H \\ (C_8H_9) \end{smallmatrix} \right\} O$	...
Rosolic acid . . . . .	$C_{12}H_{12}O_3$	...
Brunolic acid . . . . .	...	...
Ammonia . . . . .	$\left\{ \begin{smallmatrix} H \\ H \\ H \end{smallmatrix} \right\} N$	- 33
Aniline . . . . .	$\left\{ \begin{smallmatrix} (C_6H_5) \\ H \\ H \end{smallmatrix} \right\} N$	182
Pyridine . . . . .	$(C_5H_5)'''N$	115
Picoline . . . . .	$(C_6H_7)'''N$	134
Lutidine . . . . .	$(C_7H_9)'''N$	154
Collidine . . . . .	$(C_8H_{11})'''N$	170
Parvoline . . . . .	$(C_9H_{13})'''N$	188
Coridine . . . . .	$(C_{10}H_{15})'''N$	211
Rubidine . . . . .	$(C_{11}H_{17})'''N$	230
Viridine . . . . .	$(C_{12}H_{19})'''N$	251
Leucoline . . . . .	$(C_9H_7)'''N$	235
Lepidine . . . . .	$(C_{10}H_9)'''N$	260
Cryptidine . . . . .	$(C_{11}H_{11})'''N$	256
Pyrrol . . . . .	$(C_4H_5)'''N$	133
Hydrocyanic acid . . . . .	HCN	26·5

This list, however, does not indicate all the constituents of coal tar, but only those which chemists have up to the present time (1868) succeeded in separating from it; moreover, when we consider how greatly coal differs in composition, and also that the products vary according to the temperature to which the coal has been submitted, it is evident that coal tar must be an almost endless source of chemical products. Many would perhaps consider this list a perfectly hopeless jumble of names impossible to impress upon the memory; but, fortunately, chemists are able to classify their products, so that this formidable array of substances may be grouped under three or four different heads only, and, therefore, their relationship being once understood, little difficulty is experienced in remembering their names.

Amongst these products, and at the lower part of this table, you will observe a substance called "aniline." This substance is of great interest to us, being one of the principal sources of the coal-tar colours. Aniline was discovered by Unverdorben, in 1826, amongst the products of the distillation of indigo, and from its property of forming crystalline compounds with acids was called "krystalline." Afterwards Runge obtained it from the distillation of coal, and, because it gave a blue coloration with a solution of chloride of lime, called it "kyanol" or blue oil. Fritsche, still later, obtained aniline by the distillation of indigo with hydrate of potassium, and gave it its present name, derived from *anil*, the Portuguese for indigo. About this time Zinin discovered a remarkable reaction, by which he obtained aniline from a substance called nitrobenzol; he called it, however, "benzidam." The products obtained by these different chemists were not at first known to be identical; and it was not until Dr Hofmann investigated the subject that they were all shown to be the same body, aniline.

Zinin's process for the conversion of nitrobenzol into aniline consisted in treating the nitrobenzol with an alcoholic solution of sulphide of ammonium; this was greatly improved upon by Béchamp, who employed a mixture of finely divided iron and acetic acid, in place of sulphide of ammonium.

This is a brief sketch of the history of aniline up to the time of the discovery of the mauve dye; it was then purely a laboratory product, and was prepared in very small quantities at the time, and only when required for scientific research. Chemists have always been desirous of producing natural organic

bodies artificially, and have in many instances been successful. It was while trying to solve one of these questions that I discovered the "mauve." I was endeavouring to convert an artificial base into the natural alkaloid quinine, but my experiment, instead of yielding the colourless quinine, gave a reddish powder. With a desire to understand this peculiar result, a different base of more simple construction was selected, viz. aniline, and in this case I obtained a perfectly black product; this was purified and dried, and when digested with spirits of wine gave the mauve dye.

You will perceive that this discovery did not in any way originate from a desire to produce a colouring matter, as is sometimes stated, but in experiments of a purely theoretical nature.

After showing this colouring matter to several friends, I was advised to consider the possibility of manufacturing it upon the large scale, and was, eventually, induced to make the experiment, though, I must confess, not without considerable fear of the result, especially as my chemical advisers set before me anything but encouraging prospects. In starting this manufacture, the first difficulty was to decide upon the source from which aniline could be obtained at a sufficiently low price. It was at once evident that indigo was by far too costly a product for this purpose. Attention was therefore directed to the extraction of aniline from coal tar, but after very numerous experiments it was found that the difficulty of purifying it was so great, that it was not practicable to prepare it at a reasonable price from this product. There was, therefore, but one source left, namely, nitrobenzol; but to prepare aniline from this body necessitated the establishment of a new manufacture, nitrobenzol at that time not being a commercial article, and, although it could be produced in small quantities without much difficulty, yet when tons were required at a limited cost many obstacles presented themselves.

Having spoken of nitrobenzol, it will be necessary, before proceeding further, to tell you something of the body it is prepared from, and also how it is made in quantity. Nitrobenzol is produced from a derivative of coal tar called benzol—you will see it mentioned in the list of coal-tar products. It is composed exclusively of carbon and hydrogen, and is therefore called a hydrocarbon.

Benzol was discovered by Faraday, in 1825, one year before aniline by Unverdorben. Its existence in coal tar was first

pointed out by Dr Hofmann, in 1845, and afterwards Mansfield showed that an almost unlimited supply might be obtained from this source. Benzol is a volatile oil, boiling at a temperature of  $80\cdot8^{\circ}$  C., nearly twenty degrees lower than water, and is also very inflammable, burning with a smoky flame. When ignited it cannot be extinguished by water, as it floats upon its surface. Its vapour, when mixed with air, is explosive. It is also very dense. This I can easily show you by decanting a small quantity of benzol vapour several times from one vessel into another, and then igniting it. Instances have been known, when distilling benzol in large quantities, and some leak in the apparatus has occurred, so that its vapour has escaped, that it has run along the ground, and been ignited by a furnace situated thirty or forty feet distant, and instantly run back to the apparatus. To illustrate this I will pour some benzol vapour into the top of a slightly inclined trough, fourteen feet long, at the lower end of which is placed a lamp. The vapour will be seen to run gradually down till it reaches the lamp, where it ignites, and the flame instantly rushes back to the top of the trough. One of the most remarkable properties of benzol is, that when cooled down to nearly the freezing point of water, it solidifies to a beautiful crystalline mass. This property of benzol is sometimes taken advantage of when it is required in a very pure state, as the impurities which accompany it are fluid, and do not freeze when cooled with ice.

Benzol is often sold under the name of "benzine collas," for the purpose of removing grease from wearing apparel. But let us consider how benzol is separated from the great number of products with which it is associated in coal tar. The first operation consists in distilling the coal tar, just as it comes from the gas-works, in large stills, holding one or two thousand gallons each; these are often made of old steam-boilers. At first very volatile and light oily products come over, and are collected until their density increases to such an extent that they no longer float upon water. These constitute crude coal-tar naphtha. The distillation is then carried on, and heavy, or, as they are technically termed, "dead," oils are collected, a residue of common pitch being left in the still. This pitch is generally run out, and cast into blocks; but sometimes the distillation is carried on after the dead oils have been obtained, when a mixture of solid oily products distils, nothing but a kind of coke being left behind. These latter substances, however, do not interest us now.

The light oil, or crude coal-tar naphtha, is then purified by one or two alternate distillations with steam and treatments with concentrated sulphuric acid. It is thus rendered a colourless fluid. Thus purified, coal-tar naphtha contains, besides benzol, at least four or five other bodies. These, however, mostly differ from benzol in being less volatile ; therefore, the naphtha is again distilled, the first, or more volatile, portions only being collected for benzol. By repeating this process of fractional distillation several times, commercial benzol is obtained. Some manufacturers employ stills of a peculiar construction, which enable them to obtain a good product by a smaller number of distillations.

Benzol, when treated with fuming nitric acid or aquafortis, undergoes a remarkable change. At first the two fluids mix and become of a dark brown colour and slightly warm ; in the course of a few moments red fumes appear, and the mixture enters into ebullition. During this violent action the colour of the liquid becomes lighter and ultimately changes to orange. If water be now added to this product, the benzol, which is such a light body, will be seen to have completely changed into a dense yellow oil sinking in water. This oil is nitrobenzol. Nitrobenzol was discovered in 1834, by Mitscherlich. It solidifies into a crystalline mass at a temperature of about  $3^{\circ}$  C. ; its odour is like that of the oil of bitter almonds, and before the introduction of coal-tar colours it was made in small quantities, and sold under the name of *Essence de Myrbane*, for the purpose of scenting soap.

From the energy with which benzol is attacked by fuming nitric acid, nitrobenzol at first appeared to be a most difficult product to manufacture on the large scale, and this difficulty seemed the greater when it was found necessary that it should be made at a moderate cost. Moreover, at the time I am now referring to, fuming nitric acid, sp. gr. 1.5, could not be obtained in the market, or only at such a cost as almost to preclude its use. Under these circumstances, two mixtures were experimented with instead of the nitric acid in a very concentrated condition. The first was a mixture of nitrate of sodium and sulphuric acid, the second a mixture of ordinary nitric acid, sp. gr. 1.3, and sulphuric acid. The mixture of sulphuric acid and nitrate of sodium was preferred, and employed on the large scale.

The first apparatus used in the manufacture of nitrobenzol, for the preparation of aniline for the mauve dye, is shown in

fig. 1. It consisted of a large cast-iron cylinder, *a*, fitted with a stirrer, *b*, and closed with a door, *c*, fastened by a cross-bar and screw, *d*. This cylinder was capable of holding between thirty and forty gallons. It was provided with two necks, *e e* : one for the introduction of the benzol and sulphuric acid, which were supplied through a syphon tube; the other for the exit of nitrous fumes. This last was connected with an earthenware worm, to condense any benzol which might be volatilised by the heat of the reaction. The nitrate of sodium was always introduced into the cylinder before the door was fastened up and luted. Until the preparation of nitrobenzol was understood, there was a great amount of uncertainty in its manufacture, and

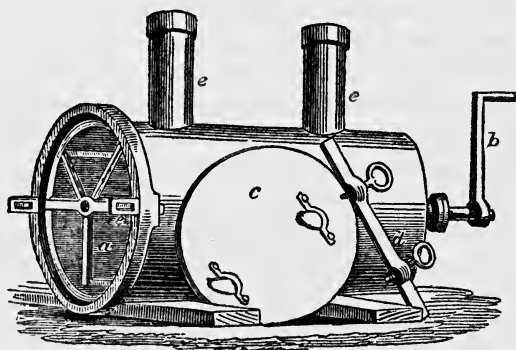


FIG. 1.

several explosions occurred, but fortunately without causing any injury to the workmen attending the apparatus. These explosions originated generally from the liberation of too much nitric acid from the nitrate of sodium, by the sulphuric acid, before the formation of nitrobenzol had begun, so that, when it started, the chemical action set in with such energy that an explosion ensued. After a few of these unpleasant occurrences, however, sufficient experience was obtained to get the manufacture under control. Apparatus of a much more extensive character has since been substituted for the cylinders.

The process of preparing nitrobenzol with a mixture of sulphuric acid and nitrate of sodium in place of nitric acid may be carried on very well in this apparatus, provided sufficient sulphuric acid be employed to produce an acid sulphate of sodium, as this will be found quite fluid at the close of the

operation, and can be freely run out at the small outlet. A mixture of strong nitric acid and sulphuric acid is now usually employed for the conversion of benzol into nitrobenzol. In working by this latter method the entire charge of benzol is first introduced through a large opening in the lid; this is then closed and the stirrer set moving; the nitric and sulphuric acids are then cautiously run in through small pipes, care being taken not to add too much nitric acid, until the red fumes begin to appear. After all the charge of acids has been added, and the reaction has perfectly ceased, the product is drawn off. At first a mixture of sulphuric and nitric acids runs out, and then the nitrobenzol; this is collected separately and purified, first by agitation with water, and then rendered perfectly neutral by means of a dilute solution of soda. Should it contain any unconverted benzol this may be distilled off by means of steam. On the Continent manufacturers do not appear to have succeeded well in manufacturing nitrobenzol when it first became a commercial article; their difficulty appears to have arisen from the fact that they experimented in earthenware vessels, which are both dangerous and unsuitable, and it was not until information was obtained from England, I believe, that they were able to produce this body at a moderate price.

We will now pass on to the processes for converting nitrobenzol into aniline. I have already mentioned that Zinin was the first who discovered that nitrobenzol could be converted into aniline, or, as he termed it, benzidam. His process consisted in treating an alcoholic solution of nitrobenzol with ammonia and sulphuretted hydrogen; but, although the discovery of this process was one of great importance from many points of view, still it was very tedious. Béchamp, however, found that by employing a mixture of acetic acid and finely divided iron instead of ammonia and sulphuretted hydrogen, the nitrobenzol was very rapidly converted into aniline, and this process has been found the best yet proposed (1868) for manufacturing aniline in large quantities. Many other reagents have been suggested, such as arsenite of sodium, powdered zinc, etc., but none of them have been found so advantageous as iron and acetic acid.

In carrying out Béchamp's process, cylinders like those used for nitrobenzol (fig. 1) were originally employed. The cylinder was set in brickwork and heated by means of a small furnace, iron borings were first introduced, and the door fixed in its place,



airtight. One neck was connected to the upper extremity of a cast-iron worm by means of a pipe called an adapter ; the second neck being fitted with a syphon-tube, for the introduction of the nitrobenzol and acetic acid. In working on the large scale it is necessary to add the nitrobenzol and acetic acid in small quantities at a time, otherwise the reaction is so violent as to almost burst the apparatus : by working carefully, however, there is no need to fear any difficulties, especially if the stirrer is well used. By the time all the charge has been introduced, a quantity of fluid will have distilled over ; this is returned into the cylinder and the fire lit, and the aniline distilled off.

The principal change which has taken place in this process consists in using high-pressure or superheated steam for the distillation instead of fire, and working the apparatus by means of a steam-engine instead of by hand.

Aniline thus obtained is generally redistilled with addition of a little lime or caustic soda, for the purpose of decomposing a body called acetanilide, which is often produced in the manufacture of aniline, especially if the operation is conducted over a fire instead of with steam.

Commercial aniline generally appears of a pale sherry colour ; when chemically pure it is colourless, but if kept long it becomes quite brown. It possesses a peculiar odour, which is slightly vinous when the aniline is pure. It burns with a smoky flame, but is not very inflammable : its boiling-point is  $182^{\circ}\text{C}$ . One of its most characteristic reactions is its power of producing a blue or blue-violet coloration with chloride of lime, to which I shall again have occasion to refer. Aniline differs entirely from benzol and nitrobenzol, being perfectly soluble in dilute acids. This is owing to its being an organic base, and forming compounds with acids. Thus with hydrochloric acid it forms hydrochlorate of aniline ; with sulphuric acid, sulphate of aniline, etc.

We will now, in a very rapid and general way, glance at the chemical changes which take place in converting benzol into nitrobenzol and aniline.

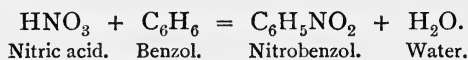
Benzol, as I have already stated, is a hydrocarbon, *i.e.* a body composed of hydrogen and carbon only ; it is represented by



This is treated with nitric acid, which contains the elements

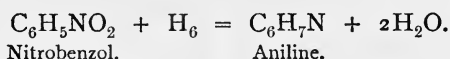


The nitric acid acts upon the benzol and introduces its nitrogen and part of its oxygen, at the same time removing hydrogen and forming water.



Nitrobenzol, when treated with iron and acetic acid, is converted into aniline by the influence of hydrogen gas, in what is termed the nascent state, or the peculiar condition in which it is when in the act of being liberated from a compound.

This hydrogen unites with the oxygen of nitrobenzol and removes it as water, and at the same time two atoms of hydrogen combine with the deoxygenated nitrobenzol, forming aniline.



Having now seen the various operations which require to be performed for the production of aniline from coal tar, we are prepared for the consideration of its coloured derivatives. We will, therefore, commence at once with the first of the coal-tar colours, the "mauve" dye. I have already given you the history of its discovery ; I will now tell you how it is made.

First of all, aniline and sulphuric acid, in the proper proportions for the formation of sulphate of aniline, are mixed in a large vat with water, and boiled until perfectly dissolved. Bichromate of potassium is then dissolved in a second large vat. These two solutions, when cold, are mixed in a third and still larger vessel, and allowed to stand one or two days. In this way a large quantity of a fine black precipitate is formed ; this is collected upon shallow filters, well washed with water, and then dried. When dry it is a most unpromising sooty-black powder, and contains various products besides the mauve ; the most troublesome of these is a brown, resinous product, soluble in most of the solvents of the colouring matter itself.

At first this resinous substance was removed by digestion with coal-tar naphtha previously to the extraction of the colouring matter, which was afterwards effected with methylated spirits of wine, and the solution thus obtained when distilled left the mauve as a fusible bronze-coloured mass.

When digesting the black precipitate with naphtha or strong spirits of wine, the operation had to be performed in closed vessels under pressure or in connection with a condensing

arrangement, otherwise large quantities of these valuable solvents would have been lost ; and great difficulty was experienced in getting apparatus perfectly tight, on account of the "searching" character of these fluids. Substitutes had also to be found for the ordinary materials employed by engineers for making good manhole joints, and a number of other matters which are apparently of but small importance, but it is remarkable the amount of difficulty and annoyance they caused. The method of extraction has, however, been materially improved upon by substituting dilute methylated spirits of wine for strong, as this weaker spirit dissolves only a small quantity of resinous matter but all the colouring matter, so that the digestion with coal-tar naphtha is now found unnecessary.

The solution of the colouring matter in dilute spirit is placed in a still and the spirit distilled off, the colouring matter remaining behind in aqueous solution ; this is filtered and then precipitated with caustic soda. It is afterwards collected on a filter, washed with water, and drained until of a thick pasty consistence, and, if necessary, dried.

The solid mauve dissolves very freely in spirits of wine, forming an intensely coloured solution ; it is also soluble to a small extent in water, but the aqueous solution on cooling forms a kind of jelly.

The formation of the mauve or aniline purple by the action of bichromate of potassium upon sulphate of aniline is a process of oxidation, and since the publication of the original specification at the Patent Office a great number of patents have been taken out for the preparation of this colouring matter, in which the bichromate has been replaced by other oxidising agents, as peroxide of lead, permanganate of potassium, peroxide of manganese, chloride of lime, ferricyanide of potassium, chloride of copper, etc. ; but I need not make any special remarks upon these various processes, as experience has shown that bichromate of potassium and a salt of aniline, the reagents first proposed, possess advantages over all others, and are now nearly universally employed for the preparation of aniline purple. The next best process appears to be that of Dale and Caro, in which chloride of copper is employed.

The affinity of aniline purple for silk or wool is very remarkable, and if I take some wool and pass it through a solution of mauve, you will see how rapidly it absorbs it, even from a

very dilute solution. Aniline purple is sent into the market in three different conditions, in paste, in solution, and in crystals ; but the latter are very rarely employed, as they are very expensive and do not offer corresponding advantages to the consumer.

The mauve is the most permanent coal-tar purple known, especially with respect to its power of resisting the action of light.

I will now endeavour to give you some idea of the approximate amount of the various products we have considered obtainable from 100 lbs. of coal, and for this purpose I have arranged them in the following table with their respective weights :—

	lbs.	ozs.
Coal . . . . .	100	0
Coal tar . . . . .	10	12
Coal-tar naphtha . . . . .	0	8½
Benzol . . . . .	0	2½
Nitrobenzol . . . . .	0	4½
Aniline . . . . .	0	2½
Mauve . . . . .	0	0¼

You see the smallness of the amount of colouring matter obtainable from coal or coal tar ; but there is fortunately one thing which, to some extent, compensates for this, and that is the wonderful intensity of this colouring matter. I will illustrate this remarkable fact. I have here a large carboy containing nine gallons of water, and will now add to this a solution containing one grain of mauve, and illuminate the liquid with the magnesium lamp, and you see the single grain has coloured this large bulk of water. A gallon of water contains 70,000 grains, therefore nine gallons contain 630,000 grains. This solution, then, contains only one part of mauve to 630,000 of water.

## II

### MAUVE, MAGENTA, AND SOME OF THEIR DERIVATIVES

Aniline purple is sometimes supplied to consumers in a pure and beautifully crystalline condition. This product is found to be a salt of a compound, chemically termed an organic base. This base has been called “mauveine” ; it is composed exclusively of carbon, hydrogen, and nitrogen, in the following proportions :



Mauveine, although the base of aniline purple, when in solution is not of a purple but of a dull violet shade, and in the solid state is a nearly black crystalline powder. The moment, however, mauveine is brought in contact with an acid so as to form a salt, its solution changes to a purple colour. This takes place even with that feeble acid, carbonic acid. I have here a dilute solution of mauveine ; you will observe the dull violet colour it possesses, but if my assistant only breathes through it a few moments the carbonic acid of his breath will combine with it, and it will acquire the ordinary colour of aniline purple.

Mauveine is a most powerful chemical body, and will easily decompose ammoniacal salts. This may be readily seen if some mauveine be heated with chloride of ammonium and a little water, when an abundance of ammonia gas will be evolved, which can be distinguished not only by its odour, but by the white fumes it produces with hydrochloric acid.

The salts of mauveine are beautifully crystalline, and possess a splendid green metallic lustre. The crystallised commercial product consists of the acetate. Mauveine possesses one of the peculiar properties of indigo. Indigo, when treated with reducing agents, such as a mixture of sulphate of iron and lime, is rendered nearly colourless and soluble, but this colourless indigo, when subjected to the oxidising influence of the atmosphere, rapidly becomes blue again. I here refer to the indigo vat so much used by dyers. Mauveine, when treated in a similar manner, is also nearly decolourised, changing to a pale brownish-yellow fluid, but the moment this is exposed to the air it assumes its original colour far more quickly than indigo. This remarkable fact may be strikingly illustrated by boiling an alcoholic solution of salt of mauveine with a few strips of zinc, in a sealed tube from which the air has been previously removed. The dark purple solution will gradually lose its colour, and change to a very pale yellowish-brown shade.

I have a tube containing some aniline purple decolourised in this manner, and now if I open it, the air rushes in and the solution instantly assumes the ordinary purple colour.

Ordinary indigo is quite insoluble in water, and, therefore, its property of becoming soluble, as well as colourless, when treated with reducing agents, is of great practical value, as the dyer, by immersing his goods in this solution of indigo, and then exposing them to the oxidising influence of the air, gets the colouring

matter firmly fixed in the fibre of his materials. But as the mauve is already soluble in water, this property has not been found of any practical value.

Aniline purple, when introduced as a dye, being the first colour of its kind, had to encounter many prejudices, and, on account of its peculiar nature, required the adoption of new or modified processes for its application. These difficulties, however, once overcome, its progress was very rapid. At first it was principally employed by the silk dyer and printer, its application to silk being comparatively easy, but it was not used by the calico-printer till a few years afterwards.

I distinctly remember, the first time I induced a calico-printer to make trials of this colour, that the only report I obtained was that it was too dear, and it was not until nearly two years afterwards, when French printers put aniline purple into their patterns, that it began to interest British printers.

It will be seen that to introduce a new coal-tar colour after the mauve was a comparatively simple matter. The difficulty in the manufacture of all the raw materials had been overcome, as well as the obstacles in the way of the practical applications of an aniline colour to the arts.

We will now turn our attention to a colouring matter which has often been confounded with aniline purple. I have designated it as "Runge's blue," as it was first observed by Runge. I have mentioned that Runge, when he first obtained aniline, termed it "kyanol," or blue oil, on account of the blue-coloured solution it gave with chloride of lime.

After discovering the mauve, I naturally made experiments with this coloured product of Runge's, to see if it contained aniline purple, but my experiments answered the inquiry in the negative. A few years afterwards, however, I was puzzled by finding that French manufacturers were beginning to produce aniline purple by the agency of chloride of lime and a salt of aniline; being much occupied at that time, I was unable to look carefully into the matter, and it was not until investigating these apparently opposite results a short time since that I was able to understand them. I will perform Runge's experiments, and for that purpose will take a solution of hydrochlorate of aniline, and add to it a very dilute solution of chloride of lime (taking care not to add too much). The solution is now changing, and getting slightly opaque; by daylight it has an appearance like

indigo, but if I render it clear by the addition of alcohol, and place it before the magnesium lamp, it is seen to be of a brilliant colour, and nearly pure blue, quite unlike aniline purple.

I have lately succeeded in obtaining this blue product in the solid condition, by treating a solution of hydrochlorate of aniline with a dilute solution of chloride of lime, and precipitating the resulting colouring matter with common salt ; it is thus obtained in an impure condition, and may be collected upon a filter ; by treatment with cold ether or benzol, a large quantity of brown impurities are separated, the colouring matter being left in the solid condition. This substance dissolves in alcohol, forming a nearly pure blue solution, and is capable of dyeing silk a blue or blue-violet colour.

An alcoholic solution of Runge's blue behaves with caustic potash quite differently from aniline purple, forming a brownish-red-coloured solution instead of a violet. Therefore, there can no longer be any reason for confounding this body with aniline purple, it being entirely different, both in colour and chemical properties. But as this colouring matter is produced by oxidising hydrochlorate of aniline with chloride of lime, how is it that manufacturers have succeeded in preparing aniline purple from the same reagents ? This question I find is very easy to answer : the manufacturer has gone a step further and boiled his product. Now, if I take a piece of silk dyed with Runge's blue, and instead of boiling it, which would wet it and make it difficult to manipulate, do that which is equivalent—steam it—a very remarkable change takes place, Runge's blue being changed into the mauve. So, here we have cleared up the mystery, and find that by the action of chloride of lime on hydrochlorate of aniline we first get Runge's blue, and then by heating this blue we change it into mauve. Runge's blue is a very unstable body, and of no practical value, its alcoholic solution changing into mauve in a day or two. This change takes place directly on boiling.

We must now pass on to another colouring matter, in name well known to all of you—I mean magenta, also called roseine, fuchsine, aniline red, and various other names. The discovery of this body and its manufacture were strangely dependent upon the source which had been selected for the preparation of aniline for the mauve. Had the aniline contained in coal tar, or the aniline obtained from indigo, been employed for the preparation



of the mauve, instead of that prepared from commercial benzol, magenta and its train of coloured derivatives would in all probability have remained unknown to this present day, from the simple fact that magenta cannot be produced from pure aniline, a second body being also required.

You will observe, by reference to the table of coal-tar products, that next to benzol there is a substance named toluol, a substance having a boiling-point not very much above that of benzol. On this account toluol is always contained in commercial benzol, and it possesses most of its properties. With nitric acid it forms nitrotoluol, very similar to nitrobenzol; with iron and acetic acid it is converted into a base, toluidine, very similar to aniline, except that it is solid instead of liquid when pure. Therefore, aniline prepared from commercial benzol always contains a little toluidine, and this is the second body requisite for the formation of magenta.

An apparatus for the fractional distillation of coal-tar naphtha has been devised, so that its constituents may be almost completely separated from each other, and thus pure benzol or pure toluol may be obtained.<sup>1</sup> Having obtained these hydrocarbons, pure aniline and pure toluidine may be prepared and then mixed in the most suitable proportions for manufacturing magenta. This process is not very generally employed, however, but the quality of the mixture of aniline and toluidine is determined by distillation, noting the quantities which come over at different temperatures. The necessity of toluidine as well as aniline for the production of magenta was discovered by Dr Hofmann, who found that it could not be produced by perfectly pure aniline, nor perfectly pure toluidine, but that a mixture of these two bases yielded it in quantity. Magenta was apparently first observed by Natanson in 1856, when examining the action of chloride of ethylene on aniline, and afterwards by Dr Hofmann in 1858, when studying the action of tetrachloride of carbon on aniline; but industrially the discovery of magenta was made by M. Verguin, of Lyons, in 1859, three years after the mauve. M. Verguin's process consisted in treating commercial aniline with a fuming liquid, called tetrachloride of tin, and was first carried out by Messrs Renard Brothers, of Lyons. Since 1859 patents have been taken out for the production of this colouring matter with aniline, and almost all chemicals known, whether capable

<sup>1</sup> See *Clarke's Eng. Pat.*, 5th June 1863, No. 1405.

or incapable of forming magenta. I may mention one process which was extensively employed, and is still used to some extent in Germany, and that is the method of making magenta with commercial aniline and nitrate of mercury. With care this process works very well, and the colouring matter produced is of good quality. When first introduced, magenta prepared by this method was not purified, but sent into the market in a crude form, so that before using it the dyer had to extract it with water. In the preparation of magenta by this process, all the mercury of the nitrate of mercury employed is recovered in the metallic state; but although this process may possess some advantages, yet the use of mercury salts is most undesirable, on account of their fearfully deleterious influence upon the workmen.

The process which has almost superseded all others involves the use of arsenic acid, as proposed by Medlock, and patented by him in January 1860. This patent is notorious for the amount of litigation it has caused, showing that a patentee should not only be a discoverer but a lawyer, and even more, and able to discover precisely how much to claim and disclaim in his patent, and also to arrange his specification so that the intellects of the whole world may not be able to discover a single flaw in his description; and it is a misfortune common to inventors who wish to thoroughly protect themselves, to find that they have claimed too much.

The manufacture of magenta, as now carried on, is a very simple process; it is conducted in an apparatus somewhat similar to that represented by fig. 2.

This apparatus consists of a large iron pot, *a*, about 4 ft. diameter, set in a furnace of brickwork; it is provided with a stirrer, *b*, worked by hand. All the gearing for this stirrer is fixed to the lid, so that stirrer, lid, and all may be lifted away by means of a crane, or other suitable apparatus. There is also a bent tube fixed into the lid, and connected to a condensing worm, *d*, by means of a joint, which can be made or broken at pleasure. In preparing magenta, a quantity of aniline, containing about 25 per cent. of toluidine, and a nearly saturated solution of arsenic acid, are introduced into this apparatus, and well mixed by working the stirrer; the proportions of the materials are in about the ratio of 1 of aniline to 1.5 of a 75 per cent. solution of arsenic acid. When these are well mixed the fire is lighted. After the product has been heated for some time, water begins

to distil over, then aniline and water, and lastly nearly pure aniline.

This operation requires some hours for completion, and this is determined by inserting an iron rod, from time to time, and drawing out a portion of the product for examination, as well as by the amount of aniline which distils over. When the heating has been completed, a steam pipe is introduced into the apparatus and steam blown through the fused mass; by this means an additional quantity of aniline is separated. The lid is then liberated and lifted, with the stirrer, from the apparatus, and the product left to cool before it is removed. A more elaborate

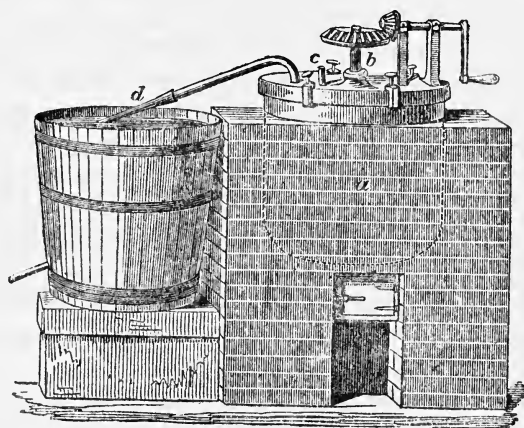


FIG. 2.

and larger apparatus is sometimes used, which possesses considerable advantages over the smaller one. The iron pot is larger, and is provided with an outlet at the side, which is closed during the operation, and the shaft of the stirrer is hollow (as in the aniline apparatus described previously), and worked by steam. When the operation of heating is concluded, steam is blown down the shaft, and after the addition of water the product is boiled and run out of the outlet in the side of the pot; by this arrangement it is unnecessary to disconnect the lid of the apparatus, and the product does not require to be removed by mechanical means, as with the apparatus described above.

The crude product obtained by heating aniline and arsenic acid is next transferred to vats, boiled with water, and filtered.

Common salt is then added, which precipitates the crude magenta; this is collected and dissolved in boiling water, again filtered, and the solution, on cooling, deposits the colouring matter in the crystalline condition. This, when recrystallised, constitutes commercial magenta.

Commercial magenta consists of brilliant crystals, sometimes half an inch in length, having a beautiful golden-green metallic appearance; these dissolve in warm water almost entirely, forming an intense purplish-red solution. Dr Hofmann has carefully studied the chemical nature of magenta, and has found it to consist of the salt of an organic base, which he has called rosaniline. This base may be obtained from the commercial product, by dissolving it in water and boiling it with an alkali, or alkaline earth, such as ammonia, potash, or lime; it is thus rendered nearly colourless, and after filtration rosaniline separates from the clear solution, on cooling, in colourless crystals. It is composed of carbon, hydrogen, and nitrogen when anhydrous, but generally contains an equivalent of water also. The anhydrous base has the formula—



This colourless base immediately becomes dark red upon combining with an acid, as I can show you by heating some with acetic acid, when the colour is immediately developed. The magenta produced by heating commercial aniline with nitrate of mercury is the nitrate of rosaniline; that produced with arsenic acid is the arseniate, but in the process of purification this latter salt becomes converted into hydrochlorate, which is the salt most generally found in the market. Other salts are also commercially manufactured, such as the oxalate and the acetate, especially when a very pure product is required; these salts are generally prepared from pure rosaniline, by combining it with the required acid, and crystallising from water.

The acetate of rosaniline crystallises in magnificent octahedra, possessing the ordinary golden-green metallic lustre to a very high degree; it is also the most soluble salt of rosaniline known. The affinity of magenta for animal fibres is very great; it does not, however, resist the action of light nearly to the same extent as the mauve. All the derivatives of rosaniline also possess a very great affinity for animal fibres, in most cases quite equal to that of magenta itself.

When speaking of aniline purple, I showed you that by reducing agents it became colourless, or nearly so, but that the original colour was developed when it was exposed to the oxygen of the air. Salts of rosaniline or magenta are also decolourised by reducing agents, but, unlike aniline purple, the colour is not restored by exposure to the air. Dr Hofmann has found that in this case a new organic base is produced which he has called leucaniline. This substance differs only from rosaniline in containing an additional quantity of hydrogen. It may be reconverted into rosaniline by oxidising agents such as bichromate of potassium, etc.

There is another very peculiar reaction of rosaniline. This base when brought in contact with hydrocyanic acid, instead of forming a coloured hydrocyanate of rosaniline, yields a perfectly colourless body, which is not a salt but a base. This remarkable fact was discovered by Dr Hugo Müller, and he has called this new body hydrocyanrosaniline. We shall have occasion to refer again to this substance and leucaniline.

In the formation of magenta, a second product is obtained, commercially called phosphine. This substance was first introduced by Mr E. Nicholson. Dr Hofmann has investigated it, and found it also to contain an organic base, which he has called chrysaniline.

Phosphine or chrysaniline is not capable of being produced at will, and the quantity formed in the manufacture of magenta is variable. In shade it is of rather a yellow orange. This colouring matter differs from rosaniline, the base of magenta, in exactly the opposite direction to leucaniline, containing two atoms less of hydrogen. Leucaniline, rosaniline, and chrysaniline are thus related :

Leucaniline	.	.	.	.	.	.	$C_{20}H_{21}N_3$
Rosaniline	.	.	.	.	.	.	$C_{20}H_{19}N_3$
Chrysaniline	.	.	.	.	.	.	$C_{20}H_{17}N_3$

The principal use of phosphine is for the formation of a scarlet with magenta. It is not converted into magenta, nor decolourised with reducing agents or hydrocyanic acid, and therefore does not seem to be of the same class of colouring matters as rosaniline.

From the residues obtained in the manufacture of magenta three new colours have been obtained by Messrs Girard and De Laire, but, I am sorry to say, my time will not allow me to

enter into the particulars of these products. I believe they have not been commercially introduced as yet.

Magenta is now more used as a source of other colours than as a dye. This has caused its manufacture to be conducted on a very extensive scale, and it is now looked upon by the manufacturer as a raw material much in the same way as aniline was regarded in the early days of aniline purple.

We will next consider some of the derivatives of magenta, and the first we will study is aniline blue or bleu de Lyon. If aniline be treated with a salt of rosaniline or magenta, a remarkable change takes place : at first the colour gradually becomes purple, but afterwards gets quite blue, ammonia being evolved at the same time. This peculiar reaction was observed by MM. Girard and De Laire, who found that this change of colour was due to the formation of a new body, which they termed the bleu de Lyon ; intermediate products were likewise obtained, to which we shall refer presently. MM. Girard and De Laire patented their process in January 1861. This new aniline blue is one of the most important of the artificial colouring matters, and its manufacture has been very much improved upon since its discovery. There are several circumstances which materially influence the beauty of its tint, such as the quality of the aniline and the particular salt of rosaniline employed in its manufacture. It is found by experience that the aniline should be as pure and free from toluidine as possible, and that the salt of rosaniline should contain a feeble acid, such as the acetate, valerate, oleate, or benzoate ; but why the latter is necessary chemists are unable to understand at present. Practically, the various salts of rosaniline required for the manufacture of the blue are not prepared separately, but are produced in the operation by double decomposition, which is simply a process of exchange ; thus, if acetate of rosaniline is required, a mixture of hydrochlorate of rosaniline and acetate of sodium is employed ; these react on each other, and change into acetate of rosaniline and chloride of sodium.

Aniline blue is manufactured in enamelled iron pots heated by an oil bath. A mixture of magenta, acetate of sodium, and aniline is introduced into the pots, the aniline being employed in excess. When charged the oil bath is heated up to  $190^{\circ}$  C., and kept near that temperature. At first the red colour of the mixture changes slowly, but afterwards with rapidity. The progress of the operation is ascertained by removing the wooden

plug, and withdrawing a small quantity of the product upon the end of an iron or glass rod, and it is considered complete when a good blue colour has been obtained ; to ascertain this point with precision, considerable experience is necessary. The excess of aniline distils during this operation, and is condensed by the worm, and collected in a suitable receiver, so that it may be used again.

From the crude blue product thus obtained, which is a fluid of the consistency of treacle, all the different qualities of blues found in the market are prepared. The cheaper qualities are obtained by simply treating the crude product several times with hydrochloric acid. This removes all the free aniline, and most of the red and purple impurities. Another similar but more effective process is employed for the preparation of the better qualities, and consists in mixing the crude product with methylated spirits of wine, and pouring it into water acidulated with hydrochloric acid, and then thoroughly washing with water the colouring matter which it precipitates. But for the purest kinds of blue there are several processes employed ; these are based upon the difficult solubility of some of its compounds in alcohol. In preparing these very pure qualities of blue, instead of starting with the crude product, one of the purified blues is taken.

Aniline blue, or “bleu de Lyon,” is supplied to consumers as a coarse powder having a coppery lustre, or in alcoholic solutions ; it is nearly insoluble in water, and has to be dissolved in alcohol before it is added to the dye bath.

The nature of this blue has been determined by Dr Hofmann. It is found to contain, like magenta, a colourless base, becoming blue only upon combining with acids. Dr Hofmann has shown this base to contain



and has called it “triphenylrosaniline.” Like rosaniline, it becomes colourless when treated with nascent hydrogen, forming a new base, giving colourless salts, as leucaniline. The composition is



The insolubility of aniline blue in water has been found a great drawback to its use, because when employed for dyeing it is thrown out of solution in the dye bath, and then mechanically adheres to the goods, so that it afterwards rubs off.

Mr Nicholson has, however, discovered a process for rendering this blue perfectly soluble in water. His process closely corresponds to that employed to render indigo permanently soluble. This, it will be remembered, is effected by subjecting indigo to the action of concentrated sulphuric acid, whereby a sulpho acid is produced.

Mr Nicholson has found that aniline blue, when treated by a similar process, also forms a sulpho acid, perfectly soluble in water, and forming with alkalis nearly colourless solutions. These, however, when decomposed by acids, change back to the original blue.

This soluble blue is now much used for silk-dyeing, but by dyers it is not thought to be so fast as the normal compound. By some modification of the process just described, Mr Nicholson has obtained another soluble blue, commercially known as "Nicholson's blue." This is now very extensively employed in Great Britain for wool-dyeing, but its application does not appear to be well understood in France and Germany, so that its use there is not so great as in our own country.

If a salt of rosaniline and aniline be heated together, and the process stopped before aniline blue is produced, the resulting product when treated with dilute acid gives a colouring matter, which has been called "violet imperial." This was at first supposed to consist of a mixture of blue and magenta, but recent research has shown it to consist of intermediate products. Very large quantities of this colouring matter have been used, but its consumption is now rapidly falling off, owing to the introduction of the new violets, about to be described. A few months after the discovery of aniline blue, another colouring matter, called the "bleu de Paris," was obtained by MM. Persoz, de Luynes, and Salvétat. These chemists found that when aniline was heated with tetrachloride of tin for thirty hours to  $180^{\circ}$  C. in a sealed tube, neither a red nor a violet, but a very pure blue, was produced. This colouring matter is generally described as being identical, or probably identical, with the "bleu de Lyon." These blues are, however, widely different in their chemical nature, as the "bleu de Paris" is easily soluble in water, and crystallises freely in needles of a blue colour, with a coppery reflection. It consists of the hydrochlorate of an organic base, which is precipitated from its solution by alkalis as a purplish-blue powder; it dyes silk readily, and retains its blue colour by



artificial light. It is remarkable that the discoverers of the "bleu de Paris" do not seem to have observed its difference from the "bleu de Lyon."

I have prepared some of this product with a view to its examination, but hitherto have been prevented from determining its composition. I hope to do so soon.

The "bleu de Paris" is, unfortunately, difficult to prepare in large quantities, and has never been introduced commercially.

The recognition of the nature of the "bleu de Lyon," by Dr Hofmann, led him to study the action of a class of substances upon rosaniline, known to chemists as the iodides of the organic radicals; this investigation resulted in the discovery of the brilliant colours known as the Hofmann violets, and of which so many shades can be obtained, from a very red purple to a nearly pure blue.

The substances generally used for the preparation of the Hofmann violets from rosaniline are the iodides of methyl and ethyl: the iodide of methyl differs from that of ethyl in a practical point of view, in being rather quicker in its action; it is also more volatile. Both these substances contain a remarkable element called iodine. This body is found in sea-water and seaweed; its aspect is very similar to that of a metal; one of its characteristic properties is that when heated it volatilises and produces a beautiful purple-coloured vapour, and here we find how dangerous a little knowledge is when relied upon. When the iodide of ethyl, which, as I have told you, contains iodine, was introduced for the preparation of the Hofmann violets, it was stated in some of our periodicals or daily papers, I do not remember which, that chemists had at last succeeded in fixing the colour of iodine, whereas the iodine has nothing whatever to do with the colours produced with the iodides of ethyl and methyl, but is simply an instrument in bringing about the change which takes place in their formation; moreover, these colours can be equally produced without using iodine at all. It is unfortunate that the popular reports upon scientific matters are generally so utterly untrustworthy. One of the most remarkable reactions of iodine is the blue-violet colour it gives with a solution of starch; this is used as a test for its presence when in the free condition, and is remarkably delicate; it is of no use as a colour, as it is instantly decomposed when heated. To prepare iodide of ethyl, ordinary alcohol is treated with iodine and phosphorus;

the operation has to be conducted with care, as iodine reacts upon phosphorus with great energy ; usually the alcohol and phosphorus are placed in a retort, and the iodine added very carefully, and in small quantities at the time. The mixture is then distilled, and the distillate mixed with water, which causes the iodide of ethyl to separate as a colourless heavy oil. Iodide of ethyl is very volatile, boiling at  $70^{\circ}$  C. ; it has an ethereal odour, and when pure is colourless and transparent ; it contains no less than 81 per cent. of iodine. Iodide of methyl is prepared in exactly the same manner as that of ethyl, substituting wood naphtha, or methylic alcohol, for ordinary alcohol ; it contains a still larger quantity of iodine than the iodide of ethyl, viz. 89 per cent.

For the preparation of these substances on the large scale special apparatus has been devised, and sometimes amorphous or red phosphorus is substituted for the ordinary kind ; but I shall not have time to enter more fully into this subject. To produce the violets, Dr Hofmann heats pure rosaniline with iodide of ethyl, or methyl and methylated spirits of wine, in a cast-iron digester, closed airtight, with a lid fastened down with screws. A process very similar to this is sometimes employed, and consists in using a salt of rosaniline, caustic alkali, iodide of ethyl, and alcohol. But in Germany the ordinary hydrochlorate of rosaniline is employed with alcohol, or wood spirit and iodide of ethyl, and is found to work very successfully. By employing the rosaniline itself a lower temperature is required for the formation of violet than when using its salts ; in fact, I have found that a mixture of iodide of ethyl and rosaniline reacts even at the ordinary temperature if left in contact for a few days, and produces a red shade of violet.

On the large scale Hofmann's violet is generally prepared in deep cast-iron vessels, surrounded by a steam jacket, and provided with a lid having a perforation, closed with a screw plug. This lid can be firmly fastened down with screws, the joint being made with a vulcanised indiarubber washer. This apparatus is charged with a mixture of hydrochlorate of rosaniline dissolved in alcohol or wood spirit, and iodide of ethyl or methyl, in proportion according to the shade required. After the apparatus is closed the steam is allowed to enter the steam jacket, and the heating continued for five or six hours ; the plug is then removed from the lid of the apparatus, and the alcohol or unused

iodide of ethyl distilled off. The resulting product is dissolved in water, filtered, and precipitated with chloride of sodium, but sometimes it is first treated with caustic alkali, to remove all the iodine, so that it may be recovered. Thus obtained, the colouring matter is of a golden lustre if of a blue shade, and of a greenish lustre if of a red shade.

Like all the other colours we have considered, the Hofmann violets are nearly white organic bases, their composition differing according to the shade of colour, thus :

A red shade is composed of	.	.	.	$C_{22}H_{23}N_3$
A red-violet shade, of	.	.	.	$C_{24}H_{27}N_3$
A very blue shade	.	.	.	$C_{26}H_{31}N_3$

The colours of the Hofmann violets are remarkable for their brilliancy, but, unfortunately, they do not resist the action of light so well as might be desired ; it is remarkable, however, that the regard for fastness seems to have given way to the desire for brilliancy.

In the early days of coal-tar colours fastness was so much talked about, that when magenta was first introduced it was thought by some that it would not be largely used—how different has it proved to be ! Although not very fast upon cotton, the Hofmann violets are sufficiently so for woollen and silk goods, as colours always resist the light better when applied to animal fibres.

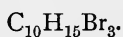
In the formation of Hofmann violets we see that rosaniline, when treated with iodide of ethyl, becomes blue, the red being converted into violet ; but with mauveine, the base of the mauve, exactly the reverse takes place, the mauveine being converted into a much redder shade with iodide of ethyl. The colouring matter produced from mauveine and iodide of ethyl is commercially known as “dahlia” ; the colour is intermediate in shade between aniline purple and magenta. The colouring matter possesses the same character for fastness as the mauve, and also gives the same reactions with acids ; unfortunately, it is rather expensive, and has therefore not been very extensively used.

Lastly, there has been a process proposed for the production of colouring matters similar to the Hofmann violets, by first converting the aniline into ethyl-aniline, a base previously discovered by Dr Hofmann. It is found that by substituting this base for aniline, in some of the processes which have been em-

ployed for the manufacture of magenta, the ethyl-aniline yields purple or violet colouring matters.

This process has been patented by MM. Poirrier and Chappat, but the reaction appears to have been first observed by M. E. Kopp. From the great similarity of these colouring matters to the Hofmann violets, I need not enter into any lengthened description of their properties.

Sea-water contains, besides iodine, another remarkable element called bromine ; it is a liquid giving off very irritating orange-coloured vapours. This remarkable body yields, with many hydrocarbons, a great variety of compounds. With ordinary turpentine, it acts with great violence ; but if the action be moderated by the presence of a large quantity of water, a thick viscid oil is obtained. This body was examined by Mr C. Greville Williams, who found it to possess the formula—



I have found that this substance, when heated with a solution of magenta in methylated spirits, produces a purple colouring matter of great beauty, commonly known as Britannia violet ; it is very extensively employed for dyeing and printing, and can be produced of any shade, from purple to a blue violet.

The Britannia violet possesses the golden-green lustre so common to all the aniline colours. It is easily fusible, amorphous, and very soluble in water.

Earlier in my lecture I showed you the great intensity of the mauve dye. I will now make a few experiments, to illustrate the great intensity of some of the colouring matters we have been considering this evening.

I have here some screens of white paper, on which I have dusted a very small quantity of the solid colouring matters—so small a quantity that I daresay you can scarcely discover its presence. If I now project spirits of wine upon these screens, so as to dissolve the colours, you will see their remarkable intensity.

Let us now consider for a moment the great rapidity with which the discovery of new coal-tar colours followed that of the mauve or aniline purple.

Aniline purple was discovered in 1856 ; three years afterwards, in 1859, the magenta was introduced. In 1861 we had the aniline blue ; in 1863 the Hofmann violet ; and in 1865

the Britannia violet. Thus we see that all these colours have not only been discovered, but introduced commercially, in a period of less than ten years.

We have now reviewed the principal coal-tar colours, but there still remain some important ones for our consideration ; and although some of these are not at present largely used, yet it is to them, perhaps, that we may look for the future development of this branch of industry.

### III

#### VARIOUS ANILINE, PHENOL, AND NAPHTHALINE COLOURS— APPLICATION OF THE COAL-TAR COLOURS TO THE ARTS

The first green colouring matter to consider is the “aldehyd green,” which owes its name to a substance called “aldehyd” being employed in its preparation. I must, therefore, first tell you what aldehyd is.

Aldehyd is a product of the oxidation of alcohol ; it is a volatile liquid possessing a very peculiar odour, and was discovered by a chemist named Döbereiner, but analysed by Liebig. It is obtained by treating alcohol with a mixture of bichromate of potassium and sulphuric acid, and was generally prepared in glass retorts, but, now that it is required for colour making, the glass apparatus is replaced by copper or leaden vessels.

Towards the end of 1861, M. Lauth described a reaction by which rosaniline could be made to produce a blue colouring matter ; but this product was found to be useless as a dye, on account of its instability. It was produced by the action of aldehyd upon a solution of rosaniline and sulphuric acid. This useless colour was afterwards experimented upon by a dyer named Cherpin, who, after a number of fruitless attempts at fixing it, told his difficulties to a photographic friend, who evidently thought if it was possible to fix a photograph it was possible to fix anything else. He, therefore, advised his confidant to try hyposulphite of sodium. On making this experiment, however, the dyer did not succeed in fixing his blue, but found it converted into a splendid green dye, now known as aldehyd green.

To prepare this colouring matter, a cold solution of magenta, consisting of one part of colouring matter dissolved in a mixture of three parts of sulphuric acid and one part of water, is em-

ployed ; about one and a half parts of aldehyd are added by degrees to this solution, and when the whole is mixed it is heated on a water bath, until a drop of the product diffused in water produces a fine blue coloration. It is then poured into a large quantity of boiling water, containing three or four times as much hyposulphite of sodium as the magenta employed. After boiling a short time the product is filtered off from a greyish insoluble residue which forms. The filtrate contains the green. This process being a very simple one, a great number of dyers now prepare the colouring matter as they require it. It may, however, be precipitated by means of tannin or acetate of sodium, collected on filters and drained to a paste, and, if necessary, dried. In both these forms it is found in the market.

The aldehyd green is principally employed in silk dyeing. It is a splendid colour, and very brilliant both by day and artificial light. The chemistry of this green is at present hidden in obscurity, as it is very difficult to obtain in a chemically pure condition. But, like the colouring matter previously described, it is undoubtedly the salt of an organic base apparently containing sulphur.

This base is colourless, or nearly so, and becomes changed to the normal colour of aldehyd green upon the absorption of carbonic acid.

It will also decompose ammonia salts, combining with the acid and becoming green. I have here a solution containing the colourless base of this green, an ammonia salt and a little free ammonia. If I pour it upon a piece of white blotting-paper it does not stain it, but if I heat it the ammonia salt is decomposed, and we get the green developed with its ordinary intensity.

There is another green of an entirely different nature to the aldehyd green ; it is called iodine green. This colouring matter is always produced, but in variable quantities, in the preparation of the Hofmann violets, from magenta and iodide of ethyl or methyl. Of late much attention has been directed to this colouring matter, and, by making a few alterations in the process for preparing Hofmann violet, from forty to fifty per cent. of product can now be obtained from the magenta used. The iodine green is much used for cotton and silk dyeing ; its colour is bluer than that of aldehyd green, and it is, therefore, more useful, as it yields, with the addition of yellow, a greater variety of green shades.

Iodine green contains an organic base which is not precipitated by alkaline carbonates. With picric acid it forms a difficultly soluble picrate, and is generally prepared on the Continent as a paste consisting of this colour precipitated with picric acid and drained on a filter. In England it is, however, sold in alcoholic solution. It is a good green by gaslight.

The next green I have to bring before you is a magenta derivative, commercially called "Perkin's green." In its properties it resembles more closely the iodine than the aldehyd green, but differs from this in its solubility, and in being precipitated by solutions of alkaline carbonates, such as carbonate of sodium. It is an organic base which is nearly colourless, and is by no means a chemically powerful body. Like the iodine green, it is precipitated by picric acid, forming a picrate which crystallises from alcohol in small prisms with a golden reflection. This colouring matter is principally employed for calico printing, and is now extensively used. Thus you see we have three aniline greens, some useful for one, and some for another purpose, so that the silk and cotton dyer and the calico-printer, as well as others, can be supplied. For fastness these greens are, I think, quite as good as the violets; the aldehyd green, however, I believe, resists light the best.

In the formation of the mauve, or aniline purple, there is always a small quantity of a second colouring matter produced, of a rich crimson colour, similar to that of safflower. Several years ago I examined this substance, and found it to dye silk a remarkably clear colour, but owing to the press of other matters, and the very small quantities in which it could be obtained, I did not give it any further attention. By a new process, however, it can now be produced in somewhat larger quantities, and endeavours are being made to introduce it to the arts, as it produces beautiful tints of pink upon silk and cotton, and, moreover, can be used for printing cotton, silk, and wool processes, to which safflower cannot be applied as it will not bear steaming. This aniline pink or crimson is a beautiful chemical body, crystallising in small prisms possessing a golden-green lustre. It is soluble in alcohol, and also in water; it produces solutions remarkable for their fluorescence—so much so, that by certain lights they appear as if filled with a precipitate. In colour and fastness it is equal to safflower, and, should it be found possible to manufacture it at a moderate price, I should

imagine it would entirely supersede that colouring matter, especially as it is not affected by alkaline solutions.

There is a product in the English market, supposed to be an aniline colour, called "Field's orange," after its discoverer, Mr Frederick Field. Its properties are those of a nitro-acid, but, as its preparation has not been described, of course I cannot tell you anything about it. With alkalis it forms a rich orange-coloured solution, but by the addition of an acid it is precipitated as a pale yellow powder.

Field's orange is a very useful colouring matter, having a great affinity for animal fibres, and is extensively used for wool-dyeing, as it resists the action of light very well.

We now come to a colouring matter of a very indefinite nature. I refer to aniline black. This substance appears to be closely allied to the insoluble part of the black precipitate formed in the manufacture of the mauve. This precipitate, however, always contains oxide of chromium, which cannot exist in the aniline black generally employed, as no chromium compound is used in its preparation; but as copper compounds are used, it may be that aniline black represents the black precipitate with the oxide of chromium replaced by the oxide of copper, or it may even be that in either case the metallic oxide is not an essential part of this black substance.

Aniline black is perfectly insoluble, and has, therefore, to be formed upon the fibre when employed for calico-printing. As we shall have to refer to its application to dyeing and printing, I will not make any further remarks upon it just now.

From mauve and magenta, chocolate, maroons and browns are prepared; but as they are of secondary importance as yet, I will only just mention one or two of the methods of preparing them.

One of the processes for preparing chocolate from magenta is by the action of nitrous acid, but care has to be taken to watch the progress of the operation, and to stop it when the required shade has been obtained. Another process consists in heating magenta with hydrochlorate of aniline to a temperature a little above  $200^{\circ}$  C. The product, when purified, produces a maroon colour. Browns are generally obtained from a residue of magenta making.

All the colouring matters we have considered up to the present time are derivatives of aniline and toluidine, and constitute nearly all the colours of the rainbow.



By the action of nascent hydrogen upon dinitrobenzol, Mr A. H. Church and myself obtained, in 1857, a crimson colouring matter, which was named nitrosophenylene. I have lately made a few new experiments upon this remarkable body, and find that it has an affinity for pure cotton, dyeing it of a clear cerise colour, considerably less blue in tint than safflower. With very dilute acids, this colouring matter forms a blue solution; with less dilute acid, a crimson colour; and with concentrated sulphuric acid, a green colour. It is difficult to judge of the probable utility of this colouring matter, as it is so difficult to obtain in quantity by the present process. I may mention that my new experiments with this substance have caused me to doubt the purity of the product examined by Mr Church and myself; and this is not remarkable when we consider how few methods of purifying artificial colouring matters were known at the date of our experiments, as well as the small amount of substances at our disposal.

We now turn to a product very different from aniline, though related to it in some respects very closely. On the table you will see a coal-tar product called "phenol" or "carbolic acid." It was discovered, a long time since, by Runge, and afterwards studied by a great number of chemists. It is only, however, during the last few years that it has been introduced into commerce in a pure condition, thanks to Dr Crace Calvert.

Phenol or carbolic acid is a splendid crystalline body, possessing many most interesting properties; but I must confine myself to a short account of its coloured derivatives only.

Carbolic acid, when treated with nitric acid, yields a yellow acid, known as picric acid. The substance can be produced from many other bodies besides carbolic acid, and when first employed for dyeing purposes was generally prepared from the resin of the *Xanthorrhoea hastilis*, but now, owing to the cheapness and purity of carbolic acid, I believe it is exclusively used in its manufacture. Picric acid requires care in its preparation, if phenol and strong nitric acid be employed, as the action is very violent. Pure picric acid is of a very pale yellow colour; it is employed principally for silk-dyeing, the colour it produces on silk being much darker than that of the acid itself. Picric acid has a very bitter taste, and by some it is said to be a great improvement upon hops in the manufacture of bitter beer, especially as it has been proposed as a tonic in place of quinine.

Picric acid forms beautiful yellow salts, the most interesting being that of potassium. This salt is extremely insoluble in water, and very explosive; it has been proposed as a substitute for gunpowder for charging shells. Picric acid, under the influence of cyanide of potassium, is perfectly decomposed, and changed into a new compound called isopurpuric acid, a substance isomeric with murexide. The potassium salt of this compound is very explosive, and, to avoid danger, it is generally supplied in a moist condition, and mixed with glycerine. It produces a kind of maroon colour upon wool, but I do not think it has been extensively used up to the present.

Runge, when experimenting with the products of the distillation of coal, obtained two compounds, called by him rosolic and brunolic acids, which he regarded as products existing in coal tar; I think it most probable, however, that these bodies were produced in his process of purification, and did not exist ready formed in coal tar.

Rosolic acid was afterwards examined by Dr Hugo Müller, who obtained it from crude carbolate of calcium, which had been exposed to the oxidising action of the air. This process, however, does not yield rosolic acid in quantity; but in 1861, Kolbe and Schmitt described a method of producing this substance, by heating a mixture of oxalic, carbolic, and sulphuric acids. It is stated, however, that this process was discovered by M. Jules Persoz, in 1859. It is by this method that rosolic acid is now manufactured.

Commercial rosolic acid, commonly called aurine, is a beautiful brittle resinous substance, having a slight green metallic lustre; when pure it may be crystallised, and if pulverised forms a scarlet orange powder. Its solutions are of an orange colour, but change with alkalis to a most magnificent crimson. It has not been found capable of very many applications in dyeing and printing, although it produces very good orange shades, and with magenta it makes a very good scarlet.

The great difficulty in applying rosolic acid to the arts is owing to the easy solubility of its salts in water. It appears to be closely allied to rosaniline, as it has lately been found possible to obtain it from this colouring matter.

When heated with ammonia, in a closed vessel, to  $120^{\circ}$  to  $140^{\circ}$  C., rosolic acid permanently changes into a new colouring matter of a crimson shade, called peonine or coralline. This

forms beautiful tints upon silk, similar to safflower, provided it is kept slightly alkaline, but if treated with the least quantity of acid the freshness of its colour is destroyed. When heated with aniline this colouring matter undergoes a similar change to magenta, being converted into a blue called azuline. This colouring matter, as well as coralline, was discovered by M. Jules Persoz, and patented by MM. Guinon Marnas & Bonnet in 1862. Azuline, when in the solid state, presents a coppery-coloured surface ; it is soluble in alcohol, but difficultly so in water. It is not manufactured now, having been replaced by the more brilliant blues obtained from rosaniline, and described previously.

We must now turn our attention to another series of coal-tar colours, derived from a beautiful product called naphthaline. You will see it on the table of coal-tar products ; it is a hydrocarbon containing



and may be obtained in any quantity. It is remarkable for the readiness with which it sublimes, and, like benzol and toluol, it yields with nitric acid a nitro-compound called "nitronaphthaline," a beautifully crystalline body, and this, with iron and acetic acid, yields an organic base called "naphthylamine." This base is solid, and beautifully crystalline, but possesses a very disagreeable odour.

Mr Church and myself obtained from a salt of "naphthylamine" and a mixture of nitrate of potassium and potash, a beautiful substance crystallising in orange needles with a green lustre. It is called by a rather long name, "azodinaphthyldiamine."

This substance is a feeble organic base, and dissolves in alcohol, forming an orange-coloured solution, which changes to a splendid violet colour upon the addition of hydrochloric acid. It has, however, been found useless as a dye, because the purple colour only exists in the presence of free acid, and the orange colour of the base itself is liable to turn brown when exposed to the light. It would appear probable, however, that azodinaphthyldiamine may become useful as the starting-point for new colouring matters, as I have lately succeeded in producing from it a very promising crimson substance, possessing a considerable affinity for animal fibres.

A very beautiful yellow colouring matter has been obtained by Dr Martius from naphthylamine, somewhat similar to picric acid, but of a much more intense colour. It is prepared by

treating hydrochlorate of naphthylamine with nitrite of potassium ; by this means a substance known as diazonaphthol is obtained ; this is then heated with nitric acid, and is transformed into the new yellow, chemically known as dinitronaphthol. This substance is commercially called Manchester yellow. It possesses the properties of an acid. The commercial compound consists of a beautifully crystalline calcium salt, soluble in water, and dyeing silk or wool a magnificent golden-yellow colour.

Owing to an increasing demand for benzoic acid, experiments have lately been made with a view of obtaining it from naphthaline instead of gum benzoin, etc. For this purpose experiments were made with an acid derived from naphthaline, called phthalic acid, which, when carefully heated with lime, is found capable of yielding benzoate of calcium, from which benzoic acid can be prepared. But as in these processes secondary compounds are formed, which interest us this evening, I will briefly describe the process employed for obtaining these various substances.

First of all, naphthaline is heated with a mixture of chlorate of potassium and hydrochloric acid ; in this way a mixture of chloronaphthaline and bichloronaphthaline is obtained. These products are then heated with nitric acid, and yield a mixture of phthalic acid and a substance called the chloride of chloroxynaphthyl. The phthalic acid is converted into the calcium salt, and heated with slaked lime to a temperature of  $350^{\circ}$  or  $370^{\circ}$  C., to convert it into a benzoate.

It is, however, the chloride of chloroxynaphthyl which interests us now. This substance, when heated with an alkali, yields the salts of an acid called chloroxynaphthalic acid, which may be obtained in a free state by means of hydrochloric acid. When pure, chloroxynaphthalic acid is a pale yellow crystalline powder, forming beautiful compounds with baryta, zinc, and copper. It dyes wool a scarlet colour. The great interest of this substance consists in its supposed relationship to alizarine, the colouring matter of madder, the only difference in composition of chloroxynaphthalic acid and alizarine being in the former containing an equivalent of chlorine in place of hydrogen, thus :



Many endeavours have been made to remove this chlorine, and to put hydrogen in its place, with the hopes of producing

alizarine ; but, up to the present time, no definite results have been obtained.

I am inclined to think that, although this relationship of composition exists between these bodies, yet that their chemical nature is quite dissimilar. We generally find that chlorinated bodies have similar properties to those from which they are derived or represent. Chloroxynaphthalic acid, however, does not appear to possess properties similar to alizarine. This acid dyes wool readily without a mordant ; alizarine only slightly stains it. When boiled with cloth prepared with alumina, or iron mordants, it scarcely produces any change, while alizarine yields intense colours.

This process of preparing benzoic and chloroxynaphthalic acids is carried out on a large scale in France, by MM. P. & E. Depouilly, to whom I am indebted for the specimens of these products shown in this lecture. Some of the chloroxynaphthalates are beautifully coloured salts, and are used as pigments.

Laurent in his researches obtained a body from naphthaline called carminaphtha. This product is now claiming the attention of manufacturers, and is said to produce very fine shades of colour upon fabrics.

Before making any further remarks upon the coal-tar colours, I wish to draw your attention to some of their applications to the arts.

I have told you that most of the coal-tar colours contain carbon, hydrogen, and nitrogen, and that they are generally organic bases. They differ essentially from most of the vegetable colouring matters, which contain, with but few exceptions, only carbon, hydrogen, and oxygen, and are weak acids. You will thus understand that many difficulties had to be encountered in their application for dyeing and printing, because they would not combine with the ordinary mordants used for the colouring matters of woods, such as alumina and oxide of tin. These observations refer to the dyeing and printing of vegetable fibres, and not to silk or wool, as these materials absorb the coal-tar colours without the intervention of a mordant.

In silk-dyeing, the principal difficulty experienced in applying the coal-tar colours was due to their great affinity for the fibre, thus preventing the dyer from obtaining an even colour, especially when dyeing light shades. After a time, however, it was found that this obstacle could be overcome by dyeing the silk in a weak

soap lather, to which the colour had been added. This not only caused the dyeing to proceed with less rapidity, but also kept the surface of the silk in good condition. Silk dyed by this process is left soft, but may afterwards be rendered hard or "scroop" by rinsing in a bath of slightly acidulated water.

This process was first used for dyeing silk with the mauve or aniline purple. It has, however, been since found suitable for nearly all the aniline colours, such as magenta, Hofmann and Britannia violets, etc. For dyeing silk with coal-tar colours of an acid nature, such as picric acid, dinitronaphthol, etc., the silk is simply worked in a cold aqueous solution of the colouring matter, sometimes slightly acidulated, as when using the sulpho acids of aniline blue or soluble blue. The process of printing silk with aniline colours is comparatively simple. An aqueous or alcoholic solution of the colouring matter is thickened with gum senegal, printed on with blocks, and, when dry, exposed to the action of steam for about half an hour. The gum is then washed off, and the goods finished.

Earlier in my lecture I referred to the formation of two colourless products from magenta, the one called leucaniline, and the other hydrocyanrosaniline.

Some few years since, it was found that if silk dyed with magenta has the reagents necessary for the formation of these colourless products printed upon it, what is called a discharge style can be produced. One of the substances used for effecting this change is powdered zinc mixed with gum. This process also applies to all the coloured derivatives of magenta, and yields better results than can be obtained by printing on the colouring matter and leaving the white parts, because the colours are always clearer when dyed than when printed. But this is not all. When printing two colours on silk, say a pattern with a green ground and purple spots, two blocks have to be used, the one for the ground and the other for the spots; and, when removing the first block, the silk often moves slightly, therefore when the spots are put in by the second block they do not exactly register, and thus an imperfect result is obtained. This difficulty, however, can be avoided by taking silk dyed with any of the derivatives of magenta, and printing it with the discharge previously mixed with the colour it is desired to introduce, of course employing a colouring matter which is not affected by the discharge, such as aniline purple, aniline

pink, etc. This discharge style has only been employed for silk at present.

We will now turn our attention to the methods of dyeing wool. These methods, as a rule, are very simple, the wool being merely worked in a hot aqueous solution of the desired colouring matter, no mordant being required. Acids are generally found to be injurious, a neutral bath being preferred, and the operation finished by bringing the temperature nearly up to that of boiling water.

With the blue known as Nicholson's blue, the process of dyeing is different from that just given, and consists of two distinct operations, the wool being first worked in an alkaline solution of the colour, which gives it a kind of grey or slate shade, and then in an acid bath, which develops the colour.

The printing of wool is similar to that of silk, the colouring matter being simply thickened with gum, printed on the goods, steamed, and then washed.

The dyeing of cotton with aniline purple at first presented many difficulties. This colouring matter was found to be capable of producing a very beautiful colour without a mordant, and it was proposed to employ it in this manner, but the colour thus obtained would not bear washing, being nearly all removed with hot water and soap. Mordants, such as alum, were then experimented with, but these gave no results. After some time Mr R. Pullar and myself found a method of applying this colouring matter to cotton, which is based upon the insolubility of the compounds it forms with tannin. In using this process the cotton is first soaked in a decoction of sumac or some other tannin agent, then in a solution of stannate of soda, and, lastly, in water slightly acidulated with sulphuric acid. The cotton thus prepared contains an insoluble compound of tin and tannin, which possesses a great affinity for aniline purple. The stannate of soda may be replaced by alum, or a solution of tin salt. This method of preparing cotton has been found suitable for nearly all the aniline colours discovered since the mauve, and is now almost universally employed in Great Britain for cotton-dyeing. Other processes have been proposed for cotton-dyeing, but are not so generally employed as the one just described.

We now pass on to the application of coal-tar colours to the art of calico-printing. The mauvé, when first introduced, was applied to printing in a very simple manner; the colouring

matter was merely mixed with gum and albumen, printed on the goods and steamed ; by this process the albumen became insoluble, and fixed the colour. Caseine and gluten were sometimes used as substitutes for albumen. Being dissatisfied with this mechanical mode of applying aniline purple, in conjunction with Mr Grey I made a number of experiments with a view of obtaining some more chemical method of fixing this colouring matter, and at last succeeded. The process proposed consisted in printing the pattern with a salt of lead, then converting this into the oxide or a basic salt, by passing the goods through an alkaline solution. Thus prepared, they were worked in a boiling solution of aniline purple in soap. In this way a very pure colour was obtained on the mordanted parts, the soap keeping the whites pure. This process, however, was of very limited application, as it could only be applied for single-colour patterns. After this, several processes were patented for the use of tannin for fixing the mauve ; these were based upon the method of dyeing cotton previously mentioned, and some very fast results were obtained ; but as these methods are now out of use, I will not describe them further.

The process now nearly universally employed in the north was discovered by M. Alexander Schultz and myself ; it consists in printing the colouring matter with a mordant composed of a solution of arsenite of alumina in acetate of alumina. On steaming the cloth printed with this mixture for about half an hour, the colour is firmly fixed in the fibre. After steaming, the goods are generally soaped, and then finished. One of the great advantages of this process is that it can be worked in patterns with a great variety of colours, and is also suitable for nearly all the aniline colours, as well as the mauve, yielding shades of great brilliancy.

During the last few years, much attention has been given to the application of aniline black in calico-printing. This substance is not prepared in the separate condition, but formed on the fabric ; it is produced by printing a mixture of a salt of aniline, chlorate of potassium, and sulphide of copper, thickened with starch, upon the goods, and in this manner a dull grey impression is obtained ; but, after three or four days' ageing, this changes to a dark olive, and is then rendered perfectly black by passing the goods through a dilute solution of carbonate of soda. This colour is very fast, but is inclined to acquire a



slightly green shade by long exposure to the air. Unfortunately, it cannot be printed on with other colours, because when steamed the cotton is destroyed by the acid character of the mixture employed for its formation. It can, however, be printed on at the same time as madder mordants, and these can be afterwards dyed with a lead mordant, so that when passed through bichromate of potassium a pattern with black and yellow or orange can be obtained.

The aniline colours have produced quite a revolution in the arts of dyeing and printing, and have made these processes far simpler than they were, and there is such a variety of shades of colour now sent into the market that the dyer or printer has little else to consider than the intensity of the colour required ; and, in fact, if a dyer has a large order to execute of a particular shade of colour not in the market, he will not trouble about matching it himself, but sends to the colour manufacturer to supply him with a product capable of yielding the required shade.

Besides dyeing and calico-printing, several other branches of industry have benefited by the coal-tar colours, such as the arts of lithography, type-printing, paper staining and colouring, etc. Before they could, however, be used for these various purposes, it was necessary that they should be made into lakes or pigments, by union with alumina or other suitable base ; but as most of the aniline colours are of a basic nature, it was found impossible to combine them directly with a metallic oxide like alumina ; advantage was, therefore, taken of their affinity for starch granules, and some very brilliant products were obtained by dyeing powdered starch with the cold aqueous solution of these colouring matters. These starch powders, however, are wanting in covering power or body, so that other processes had to be sought for, and now these lakes are made upon an alumina base, by the intervention of tannin or benzoic acid.

Many attempts have been made to prepare a pigment from rosolic acid or aurine, and this, to some extent, has been accomplished by precipitating a solution of the colouring matter with alumina ; by this process, a bright orange-scarlet-coloured product can be obtained ; it is, however, only suitable for paper-staining. I have, therefore, lately been further experimenting in this direction, and have succeeded in forming a very brilliant scarlet pigment, which can be used for printing-inks and a variety of other purposes.

Upon the table there are some specimens of magenta, Britannia violet, aniline blue, green and orange lakes, and also some very beautiful and intense-coloured preparations of coal-tar colours, now generally called carmines. These lakes, when ground with printers' varnish, produce printing-inks of very great brilliancy, and are extensively used for this purpose; and Mr Hanhart, whose name is so intimately connected with the art of lithography, has most kindly furnished me with the various illustrations of the application of these products to lithographic printing for this lecture.

These lakes in a wet condition are being largely used for paper-staining, and also for paper-colouring, as well as for a variety of other less important purposes.

The peculiar bronze surface produced by evaporating a solution of an aniline colour has been taken advantage of by the manufacturer; and all the bronze bonnets, hats, flowers, and feathers, so much worn in the autumn of last year, derived their lustre from aniline colours. When first employed for this purpose, no fixing agent was used with them; and as they are mostly soluble in water, a shower of rain was often found to cause beautiful purple drops to fall from these bronzed bonnets and hats, and produce a kind of mottled pattern upon the white collars, and sometimes even upon the face, of the wearer.

Aniline colours are used for writing-inks, colouring soap, etc.; but as these applications are only of small importance from a commercial point of view, I will not spend time in speaking about them.

I have in this lecture brought before you in a rapid—I fear too rapid—manner an account of most of the coal-tar colours; but, before concluding, I should like to show you the close relationship which exists between some of them, especially between those derived from rosaniline or magenta.

I have endeavoured to show you that the derivatives of magenta closely agree in properties, all of them containing colourless organic bases, the colour being developed upon their combining with acids. But I now wish to show you more than this, by briefly explaining their chemical structure. To describe this thoroughly it would be necessary for me to enter fully into the chemical theory of substitution; but as this would occupy a great deal of time, I must content myself with just mentioning a few facts connected with that subject.

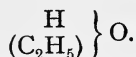
Rosaniline and its derivatives contain carbon, hydrogen, and nitrogen, as I have told you on a previous occasion. Chemical substances containing hydrogen often hold it in what is termed a replaceable condition, that is, in such a condition that it may easily be removed and another substance of equal value (either simple or compound) introduced in its place. A compound substance, capable of replacing hydrogen, is called a "radical," and I want to speak about two of these radicals, one called ethyl, and contained in iodide of ethyl, the other called phenyl, and contained in aniline.

Ethyl contains  $C_2H_5$ .  
Phenyl       ,,        $C_6H_5$ .

I will first mention a familiar instance of the replacement of hydrogen by a radical. Water is composed of two equivalents of hydrogen and one of oxygen, thus :

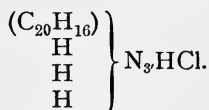


Now, it is quite easy to remove an equivalent of this hydrogen and replace it by ethyl :

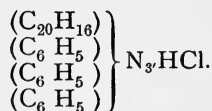


This is water with hydrogen replaced by ethyl, a replacement compound by some very much preferred to water itself ; it is alcohol.

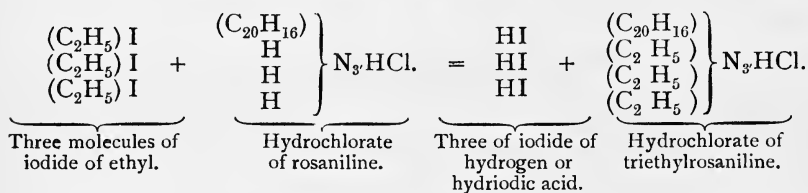
Rosaniline contains three equivalents of hydrogen, replaceable by radicals. This is the formula of the hydrochlorate of rosaniline, the three separate H's being replaceable :



Now, what takes place upon boiling this salt with aniline ? The phenyl of the aniline simply takes the place of the replaceable hydrogen, producing what is called triphenylosaniline. The result of this replacement is that the rosaniline salt has been changed from red into blue—the bleu de Lyon—which is represented thus :

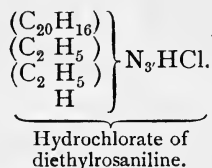


Dr Hofmann, on observing this relationship, was induced to try whether he could replace the hydrogen in rosaniline by other radicals than phenyl. He tried to introduce ethyl by digesting rosaniline with iodide of ethyl, and succeeded in introducing three molecules of the radical ethyl in the place of the three replaceable hydrogens. I will endeavour to show you how this takes place, by the following equation :—

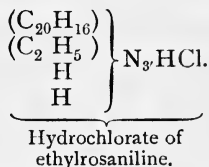


Here we see the iodine has simply exchanged its ethyl for the replaceable hydrogen of rosaniline, and the result is a blue shade of the Hofmann violet.

Now, it is not necessary to replace the three hydrogens ; two may be replaced, and we get a less blue violet. Represented thus :



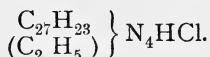
Or one may be replaced, and we get a red violet. Represented thus :



When speaking of the violet imperial, I mentioned that it consisted of products intermediate between rosaniline and the bleu de Lyon. These intermediate substances consist of rosaniline with one or two equivalents of hydrogen replaced by phenyl.

Up to the present moment it has only been found possible to replace one equivalent of hydrogen in mauveine, or the mauve dye, and, as I previously mentioned, it is curious that the result

of this replacement is perfectly opposite to that which takes place in the case of rosaniline, the replacement of hydrogen by ethyl in rosaniline causing it to become bluer in shade, and the replacement of hydrogen by ethyl in mauveine causing it to become redder in shade. The following is the formula of the hydrochlorate of ethyl-mauveine or dahlia :



But although I have tried to explain the relationship of these colouring matters as simply as I can, yet this part of my lecture assumes much of the character of a lecture on theoretical chemistry. Here we are talking about substitution products of bodies, a branch of the highest theoretical chemistry, and it must strike us as remarkable when we find that these considerations have been pressed upon us by the discussion of bodies which may now be said to be common dyestuffs. We have also been talking in quite a familiar manner about nitrobenzol, aniline, iodide of ethyl, aldehyd, etc., substances which were, only a few years since, the *recherché* compounds of the laboratory. In fact, the coal-tar colour industry is entirely the fruit of theoretical chemistry. Let us consider the enormous rapidity with which this industry has developed. It only dates from 1856, and now (in 1868) we have large factories for the production of coal-tar colours, not only in Great Britain, but in Germany, France, Switzerland, America, and other countries. I had hoped to have been able to give you a statistical account of this industry, but have not had sufficient time for this purpose. Dr Hofmann, however, in his report on the coal-tar colours shown at the Paris Exhibition of 1867, remarks that "in 1862, the value of these manufactures had risen from nothing to 10,000,000 francs, or more than £400,000 sterling. At the present day this sum is trebled, which would make it about one million and a quarter pounds sterling, although the products are much cheaper than they were before." And, now, when you hear of these results, do not forget that they are the truly practical fruits of theoretical chemistry, not studied for the purpose of producing commercial products, but simply for its own sake.

II. : 1870

## THE ARTIFICIAL PRODUCTION OF ALIZARINE

BY PROFESSOR H. E. ROSCOE, F.R.S.

(Discourse delivered at the Royal Institution, 1st April 1870)

THE discovery of artificial alizarine, whether we regard its scientific interest or its practical and commercial value, is of the highest importance, and marks an era in the history of the application of chemistry to the arts and manufactures even of greater importance than the memorable discovery made by Mr Perkin in 1856 of the production of aniline violet, or mauve.

Since the above-named year great progress has been made in the theoretical investigation of natural and artificial colouring matters, as well as in their preparation on a large scale. The chemistry of colouring matters has now taken a high and important position, and chemists, instead, as formerly was their wont, of getting rid of all colouring matters as something foreign to their objects of investigation, have, since Mr Perkin's discovery, found out that the examination of colouring matters may not only lead to scientific laurels, but may sometimes yield fruit of another and not less acceptable kind.

We owe to the brains and hands of two German chemists, Graebe and Liebermann, this remarkable discovery, which differs from all the former results which have been brought about by the application of science to the chemistry of colouring matters, inasmuch as this has reference to the artificial production of a natural vegetable colouring substance which has been used as a dye from time immemorial, and is still employed in enormous quantities for the production of the pink, purple, and black

# THE ARTIFICIAL PRODUCTION OF ALIZARINE 47

colours which are seen everywhere on printed calicoes, viz. alizarine, the colouring principle of madder.

It is from the liquid tarry products of the destructive distillation of coal, a rich source of interest to chemists, that we now derive this new colouring matter.

The following table contains the results of experiments made on a large scale, indicating the various yields of tar from different qualities of coal distilled in the gasworks of various towns :—

## DESTRUCTIVE DISTILLATION OF COAL

100 tons of cannel and bituminous coal yield the following products :—

	Gas.	Tar.	Ammonia water.	Coke.	
1	22'25	8'50	9'50	59'75	Average of many experiments. Manchester. Dukinfield. Macclesfield. Salford.
2	20'01	7'85	7'14	65'00	
3	20'40	6'4	5'4	67'85	
4	21'7	7'5	5'8	65'0	
5	16'3	10'7	8'0	65'0	

From a careful series of experiments made by a large tar distiller the following numbers are derived, showing the average composition of gas tar :—

100 tons of coal-tar on distillation yield :—

	Naphtha.	Light oils and carbolic acid.	Heavy oils, naphthalene, anthracene.	Pitch.	Water, gas, and loss.
1	3'0	1'5	35'0	50'0	10'5
2	3'0	0'8	25'0	60'0	12'2

It is from benzol,  $C_6H_6$ , discovered by Faraday in 1825, that the aniline colours are all of them prepared. The colour-producing powers of the coal products are, however, yet far from being exhausted. It is by means of another and hitherto comparatively unknown hydrocarbon, anthracene,  $C_{14}H_{10}$ , that the newest

triumphs of the chemist have been won. This is a substance which in the pure state few chemists have seen (1870), and upon which only two or three had previously experimented ; and yet by one happy discovery—and by an investigation which more than almost any other exhibits the value of the synthetic power of modern research—this unknown body has been made to yield a colouring matter of the greatest possible value. The truth of this will at once be evident when we learn that the total growth of madder is estimated to reach 47,500 tons per annum, worth £45 per ton, and having, therefore, a value of £2,150,000. Of this nearly one-half is used in the United Kingdom, so that no less a sum than £1,000,000 is now paid by us for madder grown in foreign countries. This will now, in part at least, go to benefit our own population, as we can now transform our coal into this invaluable colouring matter.

In an experiment made on a large scale it was found that 100 tons of tar yield 0·63 ton of anthracene, or 1 ton of anthracene can be obtained from the distillation of about 2000 tons of coal, not reckoning the quantity of anthracene contained in the pitch.

Madder is the root of several species of *Rubia*, amongst which the *R. tinctorium* is the most valued for its dyeing properties. This grows in Holland, Asia Minor, and in the south of France and of Russia. A species native to England is the *R. peregrina*. This belongs to the order *Rubiaceæ*, the native members of which, as the *Galiums*, are mostly inconspicuous wild plants. Some of the foreign species are, on the contrary, important plants, such as the cinchona, ipecacuanha, and coffee plants, and these are distinguished for the number and variety of the peculiar principles which they yield, as quinine, cinchonine, caffeine, alizarine. (Thanks to the kindness of Dr Schunck, the speaker was able to show a young madder plant.)

In spite of the many investigations of madder which have been made, chemists are still in doubt as to the nature of many of its constituents. Some attribute its colouring powers to the presence of at least two substances—alizarine and purpurine ; whilst others say that only one of these produces the true madder colours.

Alizarine was discovered and obtained from madder, as a crystalline sublimate, by Robiquet and Colin in 1831 ; but little importance attached to this discovery until Schunck, in 1848,



showed that all the finest madder colours contain only alizarine combined with bases and fatty acids. The second colouring matter, termed purpurine, was discovered by Persoz. It contributes to the full and fiery red colour in ordinary madder dyeing, but dyes a bad purple, alizarine being essential to the latter. Purpurine disappears during the purifying processes of soaping, etc., being far less stable than alizarine. It is distinguished from alizarine by its solubility in boiling alum liquor.

These two colouring principles may likewise be easily distinguished by their spectra, alizarine producing a set of dark absorption-bands, quite different from those of purpurine, which again vary according to the solvent. Alizarine can be obtained in yellow needle-shaped crystals by simple sublimation from the dried madder; but this colouring matter is, singularly enough, not contained ready formed in the fresh madder root, but is the product of a peculiar decomposition. For a proof that fresh madder does not contain alizarine we have only to extract the moist root with alcohol, when neither the alcoholic extract nor the insoluble residue will be found to possess tinctorial power. We owe this knowledge to the researches of Schunck and Higgin, who have proved that alizarine is produced by a peculiar kind of fermentation which partly occurs in the root on standing, and partly takes place in the dyebeck, when the powdered madder is treated with water. A crystalline glucoside, termed rubianic acid (Schunck), is contained in the root, and it is this which splits up simply into alizarine and glucose. This acid crystallises in fine yellow needles, and gives a definite and crystalline potash salt, from which it was shown to contain twenty-six atoms of carbon in the molecule. Hence, as no other product but glucose is formed, it follows that alizarine must contain  $C_{26}-C_{12}=C_{14}$ . (This decomposition of rubianic acid into alizarine was shown by boiling with an acid, and adding caustic soda, when the blue solution of alkaline alizarate was seen.) The formation of alizarine in extracts of madder root is effected by a ferment peculiar to the plant and called *Erythrozym*. It is a ferment *sui generis*, since no other ferment produces the same effect. When mixed with a solution of rubian or rubianic acid, at the ordinary temperature, the latter is rapidly decomposed as with acids. This is what takes place in making fleur de garance. Dyers raise the temperature of their madder-baths gradually up to boiling-point, because the application of a high temperature

destroys the ferment. When the temperature is gradually raised, the ferment acts upon the glucoside, and produces alizarine.

That the colouring matter in fresh madder root is not alizarine can be easily shown by rubbing the soft portions of the root on to paper, when a yellow stain will be produced, which, on treatment with an alkali, shows the bright red colour of an alkaline solution of rubian instead of the blue solution of alizarate.

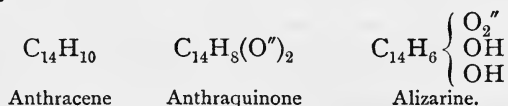
According to Schunck, the origin of purpurine, and its relation to alizarine, are still involved in obscurity.

The hypothesis which of late years has done more than any other to stimulate experiment and enlarge our views in organic chemistry is undoubtedly Kekulé's theory of the tetrad nature of carbon and his explanation of the constitution of the carbon compounds. In the so-called paraffine group of organic substances, the carbon atoms are supposed to be connected together by single links of the four bonds attached to each atom, thus giving rise to saturated compounds by the attachment of other elements or radicals to the free bonds. In the group of aromatic substances with which we are specially concerned the carbon atoms are more closely linked together, or, in other words, fewer atoms of hydrogen are necessary to saturate an aggregation of carbon atoms than is the case in the other group. We can explain this, upon the assumption of the tetrad character of carbon, by supposing that each carbon atom is attached to its neighbour alternately by one and two bonds.

Another singular property of these aromatic bodies is that they all contain at least six atoms of carbon, and that the simplest hydrocarbon of which they are made up is benzol,  $C_6H_6$ . So that we may regard all these aromatic compounds as benzol derivatives, and this hydrocarbon may be considered as the skeleton round which many complicated substances are arranged. So that by the replacement of one atom of hydrogen by  $(NH_2)$  we obtain aniline, or by  $(OH)$  phenol, etc. From the knowledge gained by the investigation on the quinones, Graebe came to the conclusion that alizarine belongs to the quinone series; and, availing themselves of Baeyer's reaction, by which phenol can be converted into its hydrocarbon benzol, Graebe and Liebermann passed the vapour of natural alizarine obtained from madder over heated zinc-dust, and found that the hydrocarbon they formed was identical in all its properties with anthracene,

$C_{14}H_{10}$ , from coal tar. Hence they confirmed Schunck's conclusions that the molecule of alizarine contained fourteen atoms of carbon. Having thus got hold of the backbone, as it were, of the compound, it only remained for them to clothe the hydrocarbon with the four additional atoms of oxygen, and to take off the two atoms of hydrogen in excess, in order to obtain alizarine.

Laurent and also Anderson had, many years ago, obtained a body of the composition  $C_{14}H_8O_2$ , and Graebe recognised this as the quinone of anthracene; and he now only required to replace in this two atoms of hydrogen by two of hydroxyl (OH), in order to obtain alizarine, which clearly appeared to be a quinone acid—



This replacement of hydrogen can be effected by bromine, by which bibromanthraquinone,  $C_{14}H_6Br_2O_2$ , is formed, and this, on fusion with caustic potash, gives potassium alizarate, yielding pure alizarine on treatment with hydrochloric acid. The high price of bromine rendered this process unavailable for manufacturing purposes, and hence another plan was simultaneously proposed by several chemists for effecting the same end in a cheaper mode. Use was hereby made of Kekulé's and Wurtz's reaction in the formation of sulpho-benzoic acid. On treating anthraquinone with strong sulphuric acid to a high temperature, the di-sulpho acid  $C_{14}H_6O_2 \left\{ \begin{array}{l} SO_3H \\ SO_3H \end{array} \right.$  is formed, and this, on heating with concentrated solution of potash, yields the sulphite and alizarate of potassium; from the latter substance pure alizarine is obtained by the action of acids.

In the following table we have a statement of the synthetic production of alizarine from its constituent elements:—

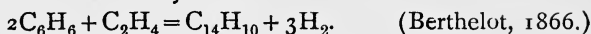
#### SYNTHESIS OF ALIZARINE

1. Acetylene by direct union of carbon and hydrogen in electric arc:
 

$C_2 + H_2 = C_2H_2.$  (Berthelot, 1862.)
2. Benzol (tri-acetylene) from acetylene by heat:
 

$3C_2H_2 = C_6H_6.$  (Berthelot, 1866.)

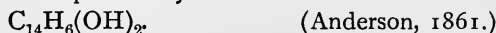
3. Anthracene from benzol and ethylene :



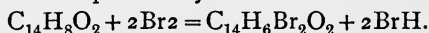
4. Alizarine from anthracene (Process No. 1).

(Graebe and Liebermann, 1869.)

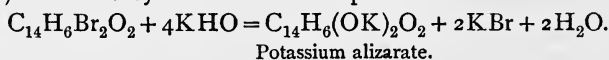
- (A) Oxyanthracene or anthraquinone by nitric acid :



- (B) Bibromanthraquinone by action of bromine :



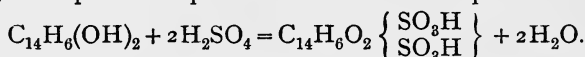
- (C) Alizarine by action of caustic potash :



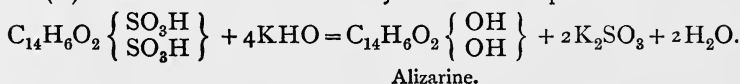
5. Alizarine from anthracene (Process No. 2) :

(Graebe and Caro, Perkin, Schorlemmer and Dale.)

- (A) Disulphoanthraquinonic acid from anthraquinone :



- (B) Alizarine from the above by the action of potash :



Mr Perkin states that an intermediate substance is formed in this reaction having the formula  $\text{C}_{14}\text{H}_6(\text{O})_2'' \left\{ \begin{array}{c} \text{OK} \\ \text{OSO}_3 \end{array} \right\}$ , and this, when heated with potash, splits up into alizarine and a sulphite. Other yellow-coloured products are, according to Perkin, contained in the alizarine as sent out from his manufactory. The nature of these yellow crystalline bodies is as yet unknown.

Of the identity of the natural with the artificial alizarine there can be no doubt ; they agree in all their physical and chemical properties. Their absorption-spectra are identical, their tinctorial powers are the same ; the coloured lakes which they form with alumina, iron, and copper salts are of the same tint and possess the same degree of solubility, and these remain alike unaltered by the action of light, so that when they are fixed in the cotton-fibre they yield equally fast colours.

It is difficult to predict how far the artificial alizarine will in future restrict the growth of madder ; but there is no doubt that for many styles of calico-printing the artificial alizarine is of the greatest value, and we may naturally expect to see very

important changes effected in this branch of chemical industry in the further practical application of this new discovery.

CONTRIBUTIONS TO THE HISTORY OF ALIZARINE,  $C_{14}H_8O_4$

- 1825. Faraday discovered benzol,  $C_6H_6$ , in coal-gas oil.
- 1831. Robiquet and Colin discovered alizarine in madder root.
- 1832. Dumas and Laurent discovered anthracene in coal oils.
- 1848. Schunck gave the composition of alizarine,  $C_{14}H_{10}O_4$ .
- 1850. Strecker gave the composition of alizarine,  $C_{10}H_6O_3$ .
- 1862. Anderson examined anthracene compounds,  $C_{14}H_{10}$ .
- 1865. Kekulé explained the constitution of the aromatic compounds.
- 1866. Baeyer obtained benzol from phenol.
- 1868. Graebe investigated the quinones.
- 1868. Graebe and Liebermann obtained anthracene from alizarine.
- 1869. Graebe and Liebermann obtained alizarine from anthracene.

III.: 1879

## THE HISTORY OF ALIZARIN AND ALLIED COLOURING MATTERS

By W. H. PERKIN, F.R.S.

(*Journal of the Society of Arts*, 1879, p. 572)

*THIS paper gives a very detailed and complete account of the history and synthetic production of alizarin. The main points are summarised in the "Hofmann Memorial Lecture" delivered by Dr Perkin before the Chemical Society in 1896, and reprinted in the present work (see p. 141).*

*The ground covered by Perkin's 1879 lecture is indicated by the following headings :—*

*History and Applications of Madder.*

*Schunck's Researches on "Natural Alizarin."*

*Graebe and Liebermann's Researches.*

*Graebe and Liebermann's First Synthesis (Bromine process).*

*The Sulphonic Acid Process (Perkin, Graebe and Liebermann, Caro).*

*Impurities in Synthetic Alizarin.*

*Alizarin Orange and Alizarin Blue.*

*The History of the Technical Manufacture of Alizarin in Perkin's works.*

*The Constitution of Alizarin.*

The concluding paragraphs only of this interesting paper are quoted :—

Having now given an account of the manufacture of artificial alizarin, it will be interesting to inquire into the commercial results of this industry, and, firstly, what has been its influence upon the sale of madder and its derivatives. I mentioned at the

commencement of this paper that the annual value of the imports into the United Kingdom, of madder and garancine, from 1859 to 1868, amounted to about £1,000,000 sterling, with prices averaging for madder 45s. to 50s. per cwt., and for garancine, 150s. In the subjoined table will be seen the remarkable changes that have taken place in the imports, and also the great reduction in price :—

AVERAGE ANNUAL IMPORTS OF MADDER AND GARANCINE  
INTO THE UNITED KINGDOM

Year.	Madder.	Garancine.	French madder.	Turkey roots.	Garancine.
	cwts.	cwts.			
1859 } 1868 }	305,840	45,560	45s.	50s.	150s.
1875	100,280	25,860	—	—	—
1876	59,137	15,396 or 6,436 }	—	—	—
1877	38,711	8,875	—	—	—
1878	32,990	2,790	18s.	17s.	65s.

Up to and during 1876 considerable quantities of artificial alizarin were imported from the Continent, and entered at the Customs as garancine or madder, and this having been brought to the notice of the officials, the returns made subsequently are more reliable. The imports of garancine were returned by the Board of Trade in 1876 as 15,396 cwts. when first published, but in the following year, when the figures for 1876 were given for comparison with those of 1877 and 1878, the returns were stated as only 6436 cwts. The erroneous entries were most probably made to evade the penalties for the infringement of patent rights.<sup>1</sup>

Dutch ground madder has been relatively much higher in price than the other qualities. This is owing to its extensive use in wool dyeing. For various reasons artificial alizarin has made but little progress in its application to wool dyeing, and

<sup>1</sup> A method so often resorted to as to render English chemical patents nearly useless as a protection against infringements by foreign manufacturers, the results of this being alike detrimental to the inventor and injurious to the national interests.

Dutch madder being mostly used for this purpose, its prices have been maintained at from 28s. for ordinary "Ombro" to about 40s. to 45s. for crop madder. The wool dyers have, however, been working cautiously with artificial alizarin, and now some of them are using it somewhat largely, and considering its cheapness as compared with Dutch madder, no doubt they will soon find how to use it successfully and cease to employ madder.

The decline in the sale of madder is still rapidly going on. During the first two months of last year the imports were—

Madder	:	:	:	:	:	6846 cwt.
Garancine	:	:	:	:	:	533 „

During the first two months of this year they were—

Madder	:	:	:	:	:	2185 cwt.
Garancine	:	:	:	:	:	175 „

or about two-thirds less. And not only so, but the price is still declining. Turkey roots may now be bought at 11s. per cwt., whereas before artificial alizarin was introduced they were sold, on an average, at 50s. At the present prices of madder, its cultivation is unremunerative, and will, undoubtedly, be soon a thing of the past. Such has been the success of artificial alizarin in competing with madder and garancine in this country, and it is equally true of other countries. The quantity of madder grown in all the madder-growing countries of the world prior to 1868 is estimated at about 70,000 tons per annum. The amount of artificial alizarin now produced is equal in dyeing power to considerably more than this; in fact, the lowest estimate I have been able to get for 1878, and which was confirmed from other sources, is 9500 tons, which is equivalent to 950,000 tons of madder. This remarkable result has been arrived at in ten years only.

To produce this quantity of artificial alizarin, there are about nine manufacturers on the Continent, and one in this country, Messrs Burt, Bolton & Haywood, who have two large works for its production, viz. the original works at Greenford Green, and new ones at Silvertown.

Graebe and Liebermann, in their paper in the *Moniteur Scientifique*,<sup>1</sup> give some statistics of the production of artificial

<sup>1</sup> *Moniteur Scientifique*, April 1879, 416.



alizarin which, however, require correcting. They also leave out the years 1869 and 1870. In 1869 we had advanced in the manufacture so far as to send colour into the market, the first invoice being dated October 4th, and that year we produced about one ton. In 1870 we produced 40 tons; in 1871, 220 tons; in 1872, 300 tons; and in 1873, 435 tons. Up to the end of 1870 we were practically the only makers of this product, one of the largest chemical and coal-tar colour manufacturing firms of Germany, with whom we were in correspondence, stating that in November 1870 they had only lately commenced producing 50 lbs. of alizarin, 10 per cent. quality, per day, and that no one else in that country was supplying artificial alizarin; and in 1871 we were practically the only producers of quantity, at any rate during the first part of the year, for in March 1871 the firm already referred to, and who had great opportunities of knowing what was being done in their country, wrote that they had not received knowledge of any establishment but their own manufacturing artificial alizarin.

In November 1871, however, Messrs Gessert Frères announced to the Industrial Society of Mulhouse that they had produced 30,792 kilogrammes of alizarin in paste. This is equal to about 30 tons, an amount which was evidently considered by them a very large quantity.<sup>1</sup>

Graebe and Liebermann's statistics are as follows compared with our production:—

	Graebe and Liebermann. Tons.	Perkin & Sons' productions. Tons.
1869 . . .	...	1
1870 . . .	...	40
1871 . . .	125-150	220
1872 . . .	400-500	300
1873 . . .	900-1000	435

Without wishing to detract from Graebe and Liebermann's original discovery, we may say, that the birthplace of the manufacture of artificial alizarin was in England. It was in this country that the difficulties and doubts about the manufacture and supply of the raw material, anthracene, were solved, and the production of artificial alizarin by new processes successfully accomplished. After these results were obtained in this country, Continental chemists were encouraged to manufacture

<sup>1</sup> *Moniteur Scientifique*, April 1879, 416.

on a comparatively large scale, but up to the end of 1873 the English manufacturers had practically no competition in the home market.

Having considered the amount of artificial alizarin now manufactured, it will be of interest to see what its money value is.

Taking the lowest estimate, viz. 9500 tons, and calculating its selling prices at £150 per ton, the annual value amounts to no less than £1,425,000, or nearly a million and a half.

As a dye, it is now at most not more than one-third of the average price of madder in 1859–1868. Consequently, in the United Kingdom, when the annual value of madder imported was £1,000,000, the annual saving is very great.

While collecting the statistics about alizarin, I thought it would be of interest to get, if possible, the statistics of the entire coal-tar colour industry, and to the kindness of H. Caro, of the Badische Anilin und Soda Fabrik, I am indebted for most of the following particulars :—

ESTIMATED VALUE OF THE PRODUCTION OF COAL-TAR  
COLOURS IN 1878

Germany . . .	£2,000,000, of which four-fifths are exported.
England . . .	450,000
France . . .	350,000
Switzerland . . .	350,000
Total . . .	£3,150,000

In referring to the works which have been set up for the purpose of making coal-tar colours, I thought it would be of interest to show a copy of a rough sketch of the first works erected for this purpose as they appeared in 1868, two years after the patent for the mauve was taken out.

These works were not one year old when sketched, and the practicability of making the mauve commercially had only been proved a short time. In 1873 they had increased to such an extent as to cover about six acres. They are represented at this date by a copy of a photograph.<sup>1</sup>

There are now in this country six coal-tar colour works ; in Germany, no less than seventeen ; in France, about five ; and in

<sup>1</sup> A copy of a photograph of the works as they appeared in 1873, and a facsimile of the sketch referred to in the text, showing the works in 1858, is given in a lithograph issued as a supplement to the *Journal of the Society of Arts*, May 30th, 1879.

Switzerland, four. There are also three works in Germany and three in France which manufacture aniline in enormous quantities for the production of coal-tar colours.

Such is the wonderful growth of this industry, which dates only from 1856. It is the fruit of scientific researches in organic chemistry, conducted, mostly, from a scientific point of view; and, while this industry has made such great progress, it has, in its turn, acted as a handmaid to chemical science, by placing at the disposal of chemists products which otherwise could not have been obtained, and thus an amount of research has been conducted through it so extensive that it is difficult to realise, and this may, before long, produce practical fruit to an extent we have no conception of. One very important colouring matter related to coal tar, and one of the original sources of aniline—a product of as great importance as alizarin—has yet to be produced on the large scale. I refer to indigo. Baeyer has shown that it can be produced artificially, but at present no practical means of accomplishing it have been discovered. No doubt, however, it will not be many years before this is achieved, and the cultivation of the indigo plant shares the fate of madder.

The Chairman, Prof. F. A. ABEL, C.B., F.R.S., said Mr Perkin had dwelt with very justifiable pride on the fact that England had been the birthplace of this particular branch of industry connected with the coal-tar colours, of which he had given the history in so lucid a manner. He had not, however, recalled to their minds that which was also true, that England was also the birthplace of the entire coal-tar industry, the development of which he had so graphically and clearly narrated. He had also, with the modesty which they all knew him to possess, forgotten to mention that he himself was the inventor and founder of this industry, which must compete in importance and interest with any other industry, either in England or any part of the civilised world.

IV.: 1880

## THE NEWER ARTIFICIAL COLOURING MATTERS DERIVED FROM BENZENE

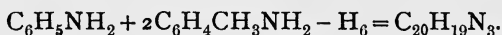
BY R. J. FRISWELL, F.C.S., F.I.C.

(*Journal of the Society of Arts*, 1880, p. 444)

### METHYL ANILINE VIOLETS

It is, no doubt, well known to many here that the earliest violets obtained by artificial means were those produced by the action of pure aniline, or phenylamine, on roseine (magenta), in the presence of an organic acid. A study of this reaction by Hofmann led to his discovery of the action of the iodides of the alcoholic radicals, methyl and ethyl, on roseine base, with the production of the well-known "Hofmann Violets." These were found to be substitution-products of rosaniline, in which one, two, or three atoms of hydrogen in the molecule are replaced by the radicals methyl or ethyl, according as the iodide of either has been used.

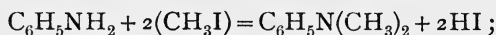
Now roseine itself is, as is well known, produced by the action of arsenic acid or other oxidising agents on a mixture of aniline and toluidine. The chemical formula then adopted for it led to the conclusion that it was produced by the coalescence of the residues of two molecules of toluidine and one of aniline, thus:—



O. and E. Fischer have recently shown that this formula was partly erroneous, and that the reaction could also occur between two molecules of aniline and one of paratoluidine—



but this does not affect the inference drawn from what was, till recently, supposed to be the constitutional formula of the body in question, and this inference was that the methylated derivatives of roseine could be obtained by the oxidation of the methylated derivatives of aniline, just as roseine was by the oxidation of aniline and toluidine. The inference was somewhat rash ; the methyl groups in dimethylaniline replace the hydrogens in the amido group, and on oxidation might, perhaps, be destroyed. However, on oxidation, dimethylaniline did, indeed, produce a very brilliant violet colour, which, having been discovered by M. Lauth, and improved and patented by Messrs Poirrier & Chappat, was introduced into commerce under the name of Paris Violet. This achievement led to a demand for the production of the methyl anilines on a large scale, and, in a very short time, this was attained. It was well known that methylaniline could be produced by the action of methyl iodide, or bromide, upon aniline, the dimethyl compound resulting from the use of two molecules of the alcoholic compound ; thus



but it was evidently necessary to produce the required compound in a cheaper way. This was eventually done by heating aniline hydrochloride and methylic alcohol together, under pressure, in strong cast-iron vessels, enamelled inside, and known as "autoclaves." Various proportions of the bodies have been employed—among others, the following giving good results :—Aniline, 33·6 ; hydrochloric acid, 37·9 ; methylic alcohol pure, 28·5 ; heat to 250° C. for eight hours. Messrs Poirrier have also employed a mixture of 100 parts aniline and 250 methyl nitrate. In the latter case, the mixture requires only a temperature of 100° C. ; but the alcoholic nitrate is an exceedingly dangerous compound to deal with ; in all probability, it was the one that led to the lamented death of Mr E. T. Chapman, and a very disastrous and fatal explosion at Messrs Poirrier's works was also caused by it.

Methylaniline is now largely made by the action of methyl chloride on aniline. As is well known, the former body has, of late years, been obtained in immense quantities in France, from a product of the destructive distillation of residues obtained in the manufacture of beet sugar. This body reacts upon aniline just as the corresponding iodide or bromide does ; it is

cheap, the reaction takes place with ease, and a remarkably pure product is produced: in fact, dimethylaniline can now be obtained by the ton, free from unaltered aniline, and containing only 3 per cent. of the monomethylated compound.

From dimethylaniline the violet is obtained by oxidation; formerly, various oxidising agents were used, among them a mixture of iodine and potassium chlorate; it is, however, now well known that very gentle oxidisers will produce the colour if a metallic salt is present, the one preferred being copper. If I heat, in this tube, some copper filings with a mixture of dimethylaniline and chloral hydrate, the whole will shortly become a mass of semi-solid violet. It is, however, obvious that so costly a method could not be employed on a manufacturing scale, and, accordingly, the following process is in very general use:—20 parts pure crystallised cupric nitrate are dissolved in 20 parts of acetic acid; some common salt is now stirred in to the mixture, which is carefully cooled down to the ordinary temperature, and 50 parts of dimethylaniline are added; the whole is then thoroughly mixed with about 250 to 300 parts of white sand, and the stiff mass thus produced is moulded into large cakes, 2 feet long by 15 inches wide, and 4 inches thick; these, arranged on copper plates, are placed in a chamber, and heated to a temperature of 60° C. for forty-eight hours. At the end of that time, they have become perfectly hard and brittle, and of a bright brassy colour. They are broken into a coarse powder and thrown into water, sulphide of sodium being added until the whole of the copper-salt has been decomposed. The mass is now washed with water and extracted with dilute hydrochloric acid at a boiling temperature. After partial cooling and filtration, to remove some resinous bye-products, the colouring matter is precipitated with common salt, and, after drying, it is ready for use. The sand, which simply serves to spread the mixture over a large surface, can be used for a fresh operation.

The product thus obtained is very brilliant in colour, and in shade is that known as 3 B, dahlia, etc.; it is, however, not the bluest that can be produced. The bluest shades are made by dissolving it in alcohol, converting it into base by the cautious addition of caustic soda, and then heating the alcoholic solution of the base with benzyl chloride—a body having the formula  $C_6H_5CH_2Cl$ , and produced by the action of chlorine on toluene. The spirit and unaltered benzyl chloride are re-

covered, and the basic colour, on conversion into the hydrochloride, is ready for use. In a similar way, by the action of methyl chloride, the well-known methyl green was produced; it is now, however, replaced by the malachite green, discovered by Oscar Doebner, and produced by the action of one molecule of benzoyl trichloride,  $C_6H_5CCl_3$ , on two molecules of dimethylaniline or of benzoylhydride, or bitter almond oil,  $C_6H_5COH$ , on the same, in the presence of zinc chloride or of sulphuric acid.

The latter colour much surpasses the former in fastness and power of standing rough treatment in the dyeing process. The methyl, and, still more, the iodine green, obtained during the manufacture of blue shades of Hofmann violet were fugitive and easily altered by heat, so that the latter could not be boiled without changing to a violet.

Before leaving the methylaniline colours, I may briefly allude to a question of scientific interest in connection with them. It is well known that Hofmann himself, at one time, considered the violets obtained by the methylation of rosaniline and those from methylaniline to be identical. On the other hand, there was much evidence against this view, for the methylaniline colour was readily rendered bluer in shade by benzyl chloride, which was almost without action on Hofmann violet; it was also more brilliant, had a much greater affinity for animal fabrics, and was less permanent when exposed to light. For these reasons, the Hofmann colour is still in demand, and, indeed, has recovered some of the ground it at first lost to the more brilliant colour. The researches of Brunner and Brandenburg, following those of Caro and Graebe, have shown that the methylaniline violets are not identical with those obtained by Hofmann's process.

#### DIPHENYLAMINE BLUE AND ALKALI GREEN

The ordinary aniline blues are obtained by the action of aniline upon roseine base, in the presence of an organic acid, at a temperature which ultimately approaches the boiling-point of the aniline used. The ultimate product of this reaction is an exceedingly intense blue, the hydrochloride of which is known as opal blue, and is, really, the hydrochloride of triphenylrosaniline. This, on dry distillation, yields diphenylamine, and the latter body, on oxidation, yields a blue which is identical with that obtained from rosaniline, but somewhat greener in shade, and is

therefore in demand for certain uses. The diphenylamine is prepared by heating, under pressure, a mixture of aniline and dry aniline hydrochloride, when the following reaction occurs :—



Diphenylamine is readily oxidised if heated with oxalic acid, and the resulting melt, purified from unaltered oxalic acid, diphenylamine, and resinous matters, is readily converted into either of the sulphonic compounds discovered by Nicholson. Blues of a redder shade can be also obtained by the oxidation of methyl- or ethyldiphenylamine.

I have now to call your attention to a green obtained from this body, discovered by Mr R. Meldola, and now under his investigation. It is obtained by the oxidation of a diphenylamine derivative. After oxidation the colour is obtained in a state corresponding to the well-known opal blue, and, like that, forms sulphonic acids. It is remarkable as being the first green obtained having this property. The sodium salt of the sulphonic acid is soluble in water, and, if wool is immersed in this solution (which is nearly colourless), and kept warm, it apparently undergoes but slight change. I have here a piece of Berlin wool which has been thus treated, and subsequently dried. You will observe that it is, apparently, only rather dirtier than undyed wool. When, however, I immerse it in warm water, acidulated with sulphuric acid, a brilliant green is immediately developed. The colour is remarkably fast ; and, since it requires exactly the same dyeing process as do the Nicholson blues for wool, one would have supposed that it would have been much liked by the dyers ; but this is not, at present, the case. It was exhibited at the late Paris Exhibition by the firm of Brooke, Simpson, & Spiller.

As time is getting on, I must now leave this very interesting field—the colours produced by the oxidation of the secondary and tertiary amines—after a very brief and incomplete glance at a few of them, and pass on to the consideration of a totally distinct group of colouring matters, which are now attracting much attention in colour-chemists' laboratories, and which have already taken an important place among artificial dyes, though, as yet, the range of shades is somewhat limited. These are obtained from substances produced by the action of nitrites on amido compounds, and are known as the azo yellows, oranges, and scarlets.



The effect of nitrites on organic compounds is very various, according to the subsequent treatment they undergo; thus, if nitrous gas is passed through a solution of diphenylamine in acetic acid, a mixture of nitroso-nitro-diphenylamines results, and this, on heating with an alkali, decomposes so far as the nitroso groups are concerned, and a mixture of mono- and dinitro-diphenylamine results, which was introduced as a yellow dye by Mr R. Meldola. A somewhat similar reaction occurs if the sulphonic acid of alpha-naphthol is similarly treated, and dinitro-naphthol may be obtained; while, if a nitrite is added to an aniline salt, and the resulting compound boiled, or if rosaniline salts are similarly treated, the whole of the nitrogen is eliminated with effervescence, and phenol in the one case, rosolic acid in the other—both of them non-nitrogenous substances—result. Before this boiling takes place, there are, however, in the two latter cases, very different bodies in solution; these bodies, which behave in the manner just mentioned on boiling, are known to chemists as “azo compounds.”

In the earlier days of organic chemistry, the prefix “azo” was applied by Mitscherlich, Laurent, Zinin, and others to many bodies containing nitrogen, such as azo-benzene,  $C_6H_5N=NC_6H_5$ , produced by the imperfect reduction of nitrobenzene, and also to others, like the compounds obtained by Laurent by the action of ammonia on bitter-almond oil and other bodies. In 1864, however, P. Griess published a magnificent memoir, in which he described a number of bodies obtained by the action of nitrous acid on aniline, and various substitution-products obtained therefrom. In this paper, he proposed that the prefix “azo” should be held to mean that the compound to which it was applied contained one atom of nitrogen occupying the place of one atom of hydrogen. This definition is now generally accepted, and thus the term “azo” has obtained a definite signification.

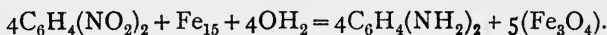
The azo compounds are, as a rule, very easily prepared; in most cases, it is only necessary to add a solution of metallic nitrite to an acid solution of a given amide, in order to obtain the diazo compound of the radicle contained in the amide; thus, if I take a solution of aniline hydrochloride, and add to it an equivalent quantity of sodium nitrite solution, the reaction at once takes place, and the diazobenzene is produced; it can be readily separated from its solution, and obtained in the solid

state, one method being to add a solution of potassium dichromate, when the chlorochromate of diazobenzene is produced. This salt, when dry, is terribly explosive, and at one time was suggested for use in warlike operations; however, it very rapidly decomposes when kept, losing nitrogen, and becoming no longer efficient.

This explosiveness is readily understood when we consider the constitution of the body which contains the group— $\text{N}=\text{N}$ —. It is manifestly in a state of unstable equilibrium, and a very slight disturbance is sufficient to bring about its decomposition; and, for the same reason, you will at once see that its chemical activity, as measured by its tendency to combine with other bodies, will be great; so that, if I add to it another molecule of aniline salt, or, what amounts to the same thing, if I add to two molecules of aniline only one of sodium nitrite, the diazobenzene formed at once attacks the free aniline salt, and what is known as diazoamidobenzene is formed, which, in the presence of an aniline salt, becomes amidoazobenzene— $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{NH}_2$ . The oxalate of this body was once in pretty general use as a yellow dye, but, as it happened to be volatile at a very low temperature, it soon evaporated from the dyed article, and was, therefore, discarded.

A compound having a very similar constitution and mode of preparation has, however, long been in use, under the name of "Bismarck brown," and is one of the most permanent of the aniline colours. It is obtained as follows:—

Metadinitrobenzene is prepared by boiling ordinary nitrobenzene with nitric acid. The compound thus produced is added cautiously, with constant agitation, to coarse iron borings, kept boiling in a large quantity of water acidulated with hydrochloric acid. A violent reaction soon commences (I could readily show you the experiment, but for the steam and unpleasant odour produced); the four oxygen atoms contained in the dinitrobenzene are replaced by hydrogen, thus:—



We have thus produced diamidobenzene, and this, when purified from a little dissolved iron, is attacked with sodium nitrite solution; the reaction here is analogous to the one last described, the final product of the reaction being a triamidoazobenzene, the hydrochloride of which constitutes the well-

known colouring matter. We have thus two terms of a possible series—first, the amido-azobenzene (yellow, volatile, and fugitive), and triamido-azobenzene (brown, and perfectly fast). Dr Witt set himself the task of filling up the intermediate link, expecting an orange colour, and a moderate stability for the diamido-azobenzene he sought. In this he was not disappointed. A study of the two compounds, from a purely scientific point of view, led him to a perfectly accurate prediction; and the discovery of “chrysoidine,” as the new colour was called, and its production—by the addition of diazobenzene chloride to a solution of diamidobenzene—was one of the first of a series of researches which have, in various hands, enriched our science and our dyers with a number of magnificent colours.

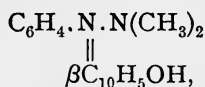
The further development of these colours commenced with the introduction of a sulphonic group into one of the amido compounds, the conversion of the sulphonic acid thus produced into a diazo body, and then using it as before; for instance, if sulphanilic acid—produced by the action of strong sulphuric acid on aniline—is converted into diazosulphanilic acid, and this added to a solution of diamidobenzene-hydrochloride, the scarlet body produced is the sulphonic acid of chrysoidine. Again, the same body will act on resorcine to produce a colour only differing from the last in that it contains hydroxyl instead of amido groups; this body has been used as a dye, under the name of tropæoline o. Witt also produced, by substituting diphenylamine for the resorcine, or diamidobenzene, another beautiful orange, known in commerce as tropæoline oo. Other compounds were subsequently prepared, and have obtained greater prominence; these were those in which a naphthol was substituted for the phenolic or amido portion of the molecule, beautiful oranges being produced by the action of diazobenzene sulphonic acid on both  $\alpha$ - and  $\beta$ -naphthol; but these colours were much improved by the introduction of sulphonic groups into both portions of the molecule,  $\alpha$ - or  $\beta$ -naphthol-sulphonic acid being, in fact, substituted for the naphthol only; still, so far, the improvement was in the direction of stability mainly, the shades still being yellow or orange; the red was yet to come.

Chemists will not be surprised to hear that the higher homologues of benzene are found, when converted into amido compounds, to give an increased redness of shade; thus, with a given phenol or amine, diazosulphotoluidinic acid, which differs from

diazosulphanilic acid by having an atom of hydrogen in the benzene ring replaced by methyl, gives redder shades than does the latter, while the substitution of another hydrogen in the same way, as is the case with the diazo compound derived from sulphoxylidinic acid, produces a scarlet. Messrs Meister, Lucius & Brüning were among the first to produce a scarlet by this method, but they also introduced both the sulpho groups into one side of the molecule—that of the naphthol. In their patent they describe the preparation of two isomeric  $\beta$ -naphthol-disulphonic acids, the sodium salts of which are differently soluble in alcohol, the most insoluble one giving a redder colour than the other. On one or other of these they act with diazoxylene chloride, produced by the action of a nitrite on xylidine chloride. The most insoluble salt above mentioned gives a scarlet closely approaching cochineal scarlet, and perfectly fast.

Mr R. Meldola has also taken out a patent for a scarlet, in which no less than three sulpho groups are engaged. He prepares diazosulphoxylidinic acid, and with this acts on  $\beta$ -naphthol-disulphonic acid; on the addition of ammonia, the colour is immediately thrown down, as you perceive. This is, after a slight purification, ready for use. By certain modifications, a scarlet, closely approaching the scarlet obtained by dyeing cochineal in the presence of oxychloride of tin, is produced.

So far, we have only oranges and scarlets by these reactions. Whether other colours can be similarly produced remains to be seen; but I may mention that Mr Meldola has recently communicated a paper to the Berlin Chemical Society, in which he describes a violet colour—unfortunately not a dye—obtained in a somewhat similar way. If we act on dimethylaniline—the body from which the violets described in the first part of my lecture are derived—with a nitrate, not an azo but a nitroso-dimethylaniline is produced, thus:— $\text{C}_6\text{H}_4\text{NON}(\text{CH}_3)_2$ . This body is as ready to combine with others as an azo body is, and does so in a very similar way, the oxygen atom being eliminated in the process, so that if we act with it on  $\beta$ -naphthol the following combination takes place<sup>1</sup> :—



<sup>1</sup> This formula is given under reserve, as a complete investigation of the compound has not yet been published.

the oxygen of the nitroso group going off with two hydrogens from the  $\beta$ -naphthol, the place of which is taken by a group, which is equivalent to azo-dimethylaniline. The colour crystallises magnificently, but its dyeing powers are very feeble.

### DISCUSSION

Mr SPILLER said it would be manifest that the benzene dye industry had of late years made gigantic strides. When he first became connected with the industry it was the rule to select out the benzole of the coal-tar and throw away a large residual product known as dead-oil. But the requirements of the latest forms of colouring matter which had been mentioned, particularly the orange and scarlet, demanded that the dead-oil should be worked up with a view to extract from it the toluene and xylene. Naphthalene had for a great number of years been a perfect bugbear in scientific industry. It was produced in immense quantities in the manufacture of gas, and, whilst by the labours of Perkin and Graebe anthracene had been employed in the manufacture of alizarin, the naphthalene had been thrown away. It was, however, now required for the manufacture of the scarlet described by Mr Friswell.

Dr H. E. ARMSTRONG said the paper ought to convey a sound lesson to the objectors to abstract science, because practically speaking the whole of these colours were the result of investigations originally undertaken without any practical aim. There was a large amount of material still remaining in coal-tar not utilised, and there was no doubt a great future in that direction.

It was not more than ten or twelve years ago that it was found that alizarin could be produced artificially, and now practically all the Turkey-red used was produced artificially. A few years ago the diazo compounds were substances which even chemists were almost afraid to handle. They were discovered by Dr P. Griess, and were extremely unstable and difficult to manipulate, and it would have appeared almost laughable that such compounds would be used for producing colouring matters on a large scale. Dr O. Witt's theoretical views with regard to the constitution of colouring matters had been very productive, and frequently enabled chemists to say, not only that a certain body would be a colouring body, but would have a certain shade.

Mr R. MELDOLA said there was no doubt that a great many of the products that now ran down our drains would one day become quite as valuable as many of those which were at present employed in factories. New diazo compounds of more and more complex constitutions were being discovered continually, and their number might increase indefinitely.

The Chairman (Prof. CHARLES GRAHAM) said that when it was remembered that Faraday discovered benzene before any of them were born, and that Unverdorben discovered aniline long ago, it was evident that there must have been much pure scientific research carried on before manufacturers were able to make use of it and convert the products of coal-tar distillation into the valuable dyeing materials we now possess.

V.: 1881

# INDIGO AND ITS ARTIFICIAL PRODUCTION

BY PROFESSOR H. E. ROSCOE, LL.D., F.R.S.

(Discourse delivered at the Royal Institution, 27th May 1881)

*THE first portion of this address deals with the various syntheses of indigotin up to the commercial introduction of ortho-nitro-phenyl propiolic acid in 1881, and with the mode of application of that body.*

Professor Roscoe proceeds as follows :—

The potential importance, from a purely commercial point of view, of the manufacture of synthetic indigo may be judged of by reference to the following statistics, showing that the annual value of the world's growth of indigo is no less than four millions sterling.

ESTIMATED YEARLY AVERAGE OF THE PRODUCTION OF INDIGO IN THE WORLD, TAKEN FROM THE TOTAL CROP FOR A PERIOD OF TEN YEARS

	Pounds weight.	Pounds sterling.
Bengal, Tirhoot, Benares, and N.W. India .	8,000,000	2,000,000
Madras and Kurpah . . . . .	2,200,000	400,000
Manilla, Java, Bombay, etc. . . . .	...	500,000
Central America . . . . .	2,250,000	600,000
China and elsewhere, consumed in the country	...	say 500,000
		4,000,000

How far the artificial will drive out the natural colouring matter from the market cannot, as has been said, be foreseen. It is interesting, as the only instance of the kind on record, to

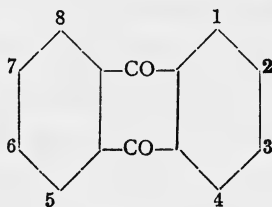
cast a glance at the history of the production of the first of the artificial vegetable colouring matters, alizarin. In this case the increase in the quantity produced since its discovery in 1869 has been enormous, such indeed that the artificial colour has now entirely superseded the natural one, to the almost complete annihilation of the growth of madder-root. It appears that whilst for the ten years immediately preceding 1869 the average value of the annual imports of madder-root was over one million sterling, the imports of the same material during last year (1880) amounted only to £24,000; the whole difference being made up by the introduction of artificial alizarin. In 1868, no less a quantity than 60,000 tons of madder-root were sent into the market, this containing 600,000 kilos of pure natural alizarin. But ten years later a quantity of artificial alizarin more than equal to the above amount was sent out from the various chemical factories. So that in ten years the artificial production had overtaken the natural growth, and the 300,000 or 400,000 acres of land which had hitherto been used for the growth of madder can henceforward be better employed in growing corn or other articles of food. According to returns, for which the speaker had to thank Mr Perkin, the estimated growth of madder in the world previous to 1869 was 90,000 tons, of the average value of £45 per ton, representing a total of £4,050,000.

Last year (1880) the estimated production of the artificial colouring matter was 14,000 tons, but this contains only 10 per cent. of pure alizarin. Reckoning 1 ton of the artificial colouring matter as equal to 9 tons of madder, the whole artificial product is equivalent to 126,000 tons of madder. The present value of these 14,000 tons of alizarin paste, at £122 per ton, is £1,568,000. That of 126,000 tons of madder at £45 is £5,670,000, or a saving is effected by the use of alizarin of considerably over four millions sterling. In other words, we get our alizarin dyeing done now for less than one-third of the price which we had to pay to have it done with madder.

Our knowledge concerning the chemistry of alizarin has also proportionately increased since the above date. For whilst at that time only one distinct body having the above composition was known, we are now acquainted with no less than nine out of the ten di-oxyanthraquinones the existence of which is theoretic-



cally possible, according as the positions of the two molecules of hydroxyl are changed.



Of the nine known di-oxyanthraquinones, only one, viz. alizarin, or that in which the hydroxyls are contained in the position 1, 2, is actually used as a colouring agent. Then again, three tri-oxyanthraquinones,  $C_{14}H_5O_2(OH)_3$ , are known. One of these is contained in madder-root, and has long been known as purpurin. The other tri-oxyanthraquinones can be artificially prepared. One termed anthrapurpurin is an important colouring matter, especially valuable to Turkey-red dyers, as giving a full or fiery red. The other, called flavopurpurin, gives an orange dye with alumina mordants. All these various colouring matters can now be artificially produced, and by mixing these in varying proportions a far greater variety of tints can be obtained than was possible with madder alone, and thus the power of diversifying the colour at will is placed in the hands of the dyer and calico-printer.

It is quite possible that in an analogous way a variety of shades of blue may be ultimately obtained from substituted indigos, and thus our catalogue of coal-tar colours may be still further increased.

To Englishmen it is a somewhat mortifying reflection, that whilst the raw materials from which all these coal-tar colours are made are produced in our country, the finished and valuable colours are nearly all manufactured in Germany. The crude and inexpensive materials are, therefore, exported by us abroad, to be converted into colours having many hundred times the value, and these expensive colours have again to be bought by English dyers and calico-printers for use in our staple industries. The total annual value of manufactured coal-tar colours amounts to about three and a half millions; and as England herself, though furnishing all the raw material, makes only a small fraction of this quantity, but uses a large fraction, it is clear that she loses the profit on the manufacture. The causes of

this fact, which we must acknowledge, viz. that Germany has driven England out of the field in this important branch of chemical manufacture, are probably various. In the first place, there is no doubt that much of the German success is due to the long-continued attention which their numerous universities have paid to the cultivation of organic chemistry as a pure science. For this is carried out with a degree of completeness, and to an extent, to which we in England are as yet strangers. Secondly, much again is to be attributed to the far more general recognition amongst German than amongst English men of business of the value, from a merely mercantile point of view, of high scientific training. In proof of this it may be mentioned, that each of two of the largest German colour-works employs no less a number than from twenty-five to thirty highly educated scientific chemists, at salaries varying from £250 to £500 or £600 per annum. A third cause which doubtless exerts a great influence in this matter is the English law of patents. This, in the special case of colouring matters at least, offers no protection to English patentees against foreign infringement, for when these colours are once on the goods they cannot be identified. Foreign infringers can thus lower the price so that only the patentee, if skilful, can compete against them, and no English licensees of the patent can exist. This may to some extent account for the reluctance which English capitalists feel in embarking in the manufacture of artificial colouring matters. That England possesses both in the scientific and in the practical direction ability equal to the occasion, none can doubt. But be that as it may, the whole honour of the discovery of artificial indigo belongs to Germany and to the distinguished chemist Professor Adolf Baeyer, whilst towards the solution of the difficult problem of its economic manufacture the first successful steps have been taken by Dr Caro and the Baden Aniline and Soda Works of Mannheim.

VI.: 1885

## THE COLOURING MATTERS PRODUCED FROM COAL-TAR

BY W. H. PERKIN, F.R.S.

(Presidential Address, Society of Chemical Industry, 1885:  
*Jour. Soc. Chem. Ind.*, 1885, p. 426)

TAKING a precedent from some of those who have occupied this chair before me, I have selected for my few remarks to-day the subject in relation to Technical Chemistry, with which I have been personally connected—namely, the colouring matters produced from coal-tar products, with some of the lessons its development appears to me to teach us in connection with industrial chemistry. Sir Frederick Abel, in his address in 1883, when speaking of the history of gunpowder, said that “It is one of the most remarkable features connected with the history of gunpowder, that until the last quarter of a century no radical changes should have been introduced into the manufacture and modes of applying this, the first known practically useful explosive agent.” It appears to me that this is more or less true of all the older industries, which resulted simply from experiment and observation without any other basis to work from. They have had long histories in which little progress has been made, but of late years, owing to our advanced and rapidly increasing scientific knowledge, they are undergoing great, and in many cases radical, changes.

The coal-tar colour industry stands in a very different position to our older ones. It has a sharply defined origin, and a very short history dating back only to 1856, and it is not yet twenty-nine years since the date of the first patent. It is an industry which has been founded on scientific discovery, and has developed side by side with it, being in fact a most important handmaid to research,

which in its turn has repaid it by new discoveries. At the date of its introduction very little was known of the chemistry of colouring matters; they were always found difficult bodies to investigate, and when produced in reactions were generally regarded as secondary products, and every endeavour was made to get rid of them so that the other products associated with them might be examined; but now, owing to the very extended study which has been made of these bodies, on account of this industry, and the relationships which have been found to exist between the colour of the compounds and the chemical constitution, it is possible with more or less certainty to predict the colour a compound will have before it is produced, and the means which can be used to modify it.

It will be possible for me to give you only a very brief sketch of the history of this industry in the time at my disposal; anything like a complete account would fill volumes. On account of this I shall not be able to refer except casually to the coal-tar industry itself, the development of which is mainly due to the one under consideration. Nor can I give a consecutive account of the coal-tar colours themselves, because the discovery of new series of colouring matters, and the progress of old ones, necessarily produce overlapping as it were, and renders such a course difficult and confusing. I therefore propose to take them according to the groups we now know them to belong to. I will therefore commence with that which contains the first colouring matter connected with this industry—*i.e.* the mauveine and safranine group of compounds.

As I already mentioned, the coal-tar colour industry dates from 1856, the discovery of the aniline purple or mauve dye being made during the Easter vacation of that year, and the patent for its production taken out on the 26th of the following August. I have already described elsewhere<sup>1</sup> how the discovery of this colouring matter was made during the prosecution of scientific research which had for its object the artificial production of quinine, a subject which of late has very much occupied the attention of chemists, though it has not as yet been accomplished.

When commencing this industry, which was looked upon by many with considerable doubt as to its practicability, the difficulties encountered were very numerous on account of its unique character, but few of the processes having their representatives

<sup>1</sup> See p. 5, *ante*.

in other industries ; the products were also very valuable, so that great care had to be employed with them. Moreover, the success of the product tinctorially had not been proved on the large scale, so that it was necessary to proceed tentatively and not launch out too rapidly.

Aniline, as is well known, was at this period a rare body, originally obtained from indigo by Unverdorben in 1826 ; for its production from benzene we are first indebted to the discovery of nitrobenzene in 1834 by Mitscherlich, and then to Zinin, who found that this substance when submitted to certain reducing agents produced a base which was eventually identified as aniline. It was not long before the date of this industry that a method of producing this base from nitrobenzene, with greater ease than by the process of Zinin, was discovered ; and it is to Béchamp we are indebted for this, who found that the reduction might be easily accomplished by means of iron filings and acetic acid. Had this discovery not been made, aniline could not have been produced sufficiently cheap to be used for the production of colouring matters. And it is interesting to note that this process of Béchamp, slightly modified, is the one used to-day for the production not only of this base, but its homologues and analogous compounds.

It was not long before the difficulties of producing nitrobenzene were to a great extent overcome. Messrs Simpson, Maule & Nicholson also began to experiment on the production of nitrobenzene, and after a time were able to produce it at a sufficiently low cost to be able to supply us with part of our requirements. I mention this in passing because it was the starting-point of the history of the connection of this firm with artificial production of colouring matter, which they carried on so successfully afterwards.

After the mauve was discovered it was necessary to teach dyers how to use it. Being an organic base, it is opposite in properties to the vegetable colouring matter, and therefore the ordinary methods of application were not generally useful, and much time had to be spent in dye-houses and print-works in the early days of this product in reference to this subject, and at that time the question of fastness to light, soap, and bleaching liquor was much insisted on. Fortunately for the future of the coal-tar colour industry, although the mauve would not resist bleaching liquor well, it proved to be a very fast colour—the fastest purple

yet produced, I believe—and thus its introduction became rapid. After this the love of brilliancy of colour which it had induced caused less attention to be given to the subject of fastness. I quite think that had this, the first coal-tar colouring matter, yielded colours as fugitive as some which have since been used, this industry would probably have been, to say the least, much delayed in its progress; so that it will be seen the mauve had to bear all the burdens of the difficulties incident on the inauguration of this industry, the future products being free from these impediments. The importance of this colouring matter after its success was established was quickly recognised in France, and its manufacture commenced there. This soon resulted in its importation into this country irrespective of patent rights. As, however, the foreign manufacturer employed responsible agents in this country, the law was without difficulty put into operation successfully—unfortunately, however, only to teach Continental manufacturers the lesson not to employ responsible agents in this country any longer, but, by means of correspondence or travellers to deal directly with the consumers, and this *modus operandi* (practically, though perhaps not theoretically) enabled them to ignore the existence of patents, and import their products freely into this country. On this point I shall have to speak again further on. The mauve was first employed in silk dyeing in London, Messrs Thomas Keith & Sons, of Bethnal Green, being the first to use it. The second application was calico printing, Messrs James Black & Co., of Glasgow, being the first to employ it largely for this purpose. It afterwards was extended to other trades.

With reference to the chemical history of this dye, although it had been submitted to analysis very soon after its discovery, its formula, or rather the formula of its principal constituent “mauveine,” was not established until some time after it had become a commercial product, and was prepared in a crystalline condition. It was then shown to have the composition  $C_{27}H_{24}N_4$  (*Proc. R.S.*, xiii. 170).

It was found to be a very powerful base, decomposing ammonia salts with evolution of ammonia, and combining with carbonic acid to form a carbonate. Its ordinary salts are produced by its combination with one molecule of a monobasic acid, its hydrochloride having the formula  $C_{27}H_{24}N_4HCl$ .

In concentrated sulphuric acid mauveine dissolves with a dirty

green colour, changing to blue on slight dilution, and back to purple when thoroughly diluted ; this is a distinctive reaction of this class of colouring matters. Further researches have shown (*Jour. Chem. Soc.*, xxxv. 717-732) that in the ordinary commercial product, besides mauveine, there are two other compounds, one possessing a redder shade of colour, the other being remarkable for its great solubility in alcohol. This latter from analysis appears to have the formula  $C_{24}H_{20}N_4$ .

The first product, or mauveine, is evidently a derivative of paratoluidine and aniline. The second of orthotoluidine and aniline, and the third of pure aniline. This has been called pseudo-mauveine. It might perhaps be better called pheno-mauveine.

When boiled with aniline mauveine yields an indigo-blue product, difficultly soluble in alcohol. This change takes place without formation of ammonia, and shows how different mauveine is in its character to rosaniline.

Runge found that aniline, when treated with dilute chloride of lime, yielded a blue- or violet-coloured solution, which soon underwent change. Some experiments on this, made in 1868 (*Jour. Chem. Soc.*, xxii. 25-27), showed that the product which I named "Runge's blue" was a peculiar compound, the salt of an organic base, which itself dissolved in alcohol with a reddish-brown colour, the salts being blue. It is quite different from mauveine, and of no practical value ; but what is interesting is that when exposed to heat, as by boiling a solution of one of its salts, it decomposes with formation of mauveine.

A beautiful colouring matter was obtained from mauveine by treating it with ethyl iodide. It gives shades of colour of a very red purple tint, and it was therefore called dahlia. It was mostly used in calico delaine and other kinds of printing, but being costly, the production was never very large. This substance is a monoethyl derivative of mauveine, and all attempts to further ethylate this compound have proved fruitless. In properties it appears to be more like an ammonium compound than a displacement product.

#### SAFRANINES

In the preparation of mauveine, a colouring matter was obtained from the liquors, from which it was precipitated,

yielding beautiful crimson-red shades of colour on silk. The amount produced in this was so small, however, that we were not able to introduce it as a dye. But it was found that it could be produced by the oxidation of the mauve dye itself, and was then manufactured under the name of "aniline pink," but afterwards "safranine." This substance is evidently closely related to mauveine, as it gives the characteristic reaction with sulphuric acid I have already referred to.

The preparation of this from the mauve dye was too costly to allow of its being brought into general use. However, new processes have been since discovered, by which this and other colouring matters of its class can be produced cheaply.

The first of these processes consisted in passing nitrous acid into commercial aniline, heating the mixture with arsenic acid, and then extracting the colouring matter produced. Hofmann examined this, and showed that it had the formula  $C_{21}H_{20}N_4$  (*Ber.*, vi. 526, 1872).

By examination of the product which was obtained by oxidising the mauve dye I found it to have the composition  $C_{20}H_{18}N_4$  (*Jour. Chem. Soc.*, xxxv. 731), results which correspond with analyses published by Dale and Schorlemmer (*Jour. Chem. Soc.*, xxxv. 682) obtained from the examination of a similar product. This substance, I also found, was associated with that examined by Hofmann in a product prepared by Messrs Guinon & Co., of Lyons.

Methods of a more synthetical nature have since then been discovered. O. Witt found that safranine could be obtained from orthoazotoluene and hydrochloride of toluidine at  $150^{\circ}$ – $200^{\circ}$  C. (*Ber.*, x. 874, 1877). He then found that by oxidising a mixture of one part of paraphenylenediamine, and two parts of aniline, on the application of heat a safranine could be obtained which has the formula  $C_{18}H_{16}N_4$ , and which is called phenosafranine.

The formation of this colouring matter by this and other processes has been studied by Nietzki (*Ber.*, xvi. 464). He finds that the aniline in the reaction, in which paraphenylenediamine takes part, may be substituted by other primary monamines, or a mixture of these with dimethylaniline, and thus a large number of these dyes can be obtained.

Phenosafranine is now produced very largely, and in a pure crystallised condition, and is a very useful dyeing agent.



If we assume that all the safranines are strictly homologous compounds, the formula that Nietzki gives for phenosafranine would make the formula of that examined by Hofmann, and that examined by myself and Dale and Schorlemmer, to be incorrect, and that they should contain two hydrogens more than are assigned to them. This I cannot think is possible from all the analytical results we obtained.

The constitution of mauveine has not yet been established, and I have still experiments on this subject in hand. This may also be said of safranine, I think, although Nietzki has proposed a formula for it in which nitrogen occupies a similar position to the methane-carbon in the rosaniline series.

### TRIPHENYLMETHANE DERIVATIVES

We must now go back again to the early days of this industry to consider the next class of compounds—viz. triphenylmethane derivatives.

The industrial success of the mauve dye caused aniline to become a very favourite body to experiment with, and the result was that in 1859 the discovery of that important colouring matter first known as fuchsine or magenta took place. Hofmann had observed in his experiments on the action of carbon tetrachloride on aniline in 1858 the formation of a red colouring matter, which consisted of this substance as a secondary product of the reaction, but it was M. Verguin who first discovered a process for the transformation of aniline into a red colouring matter of tinctorial value. The discovery of this compound marks a most important fresh departure in the history of coal-tar colours. As I mentioned, the mauve had paved the way for future colouring matters, and this new substance, which could be applied to fabrics by the same methods as the mauve, was most eagerly sought after owing to the brilliancy of its colour, and probably its manufacture was one of the most successful financially of all the aniline colours.

M. Verguin's process, which consisted in treating commercial aniline with tin tetrachloride, was soon superseded by better processes. The number of patents taken out for the production of this dye was very large, and all imaginable products were claimed as capable of producing it from aniline. The two most important, however, were those in which mercury nitrate and

arsenic acid were used. The first of these processes, with which I had some experience, required much care to regulate the reaction and prevent deflagration. The next process with arsenic acid, known as Medlock's, was by far the best, and was employed very extensively until the last few years, nitrobenzene being now mostly used as the oxidising agent in the place of arsenic acid.

The manufacture of magenta, which at this period was often called roseine, was carried on chiefly in this country by Messrs Simpson, Maule & Nicholson, by the arsenic acid process. Mr E. C. Nicholson and Dr A. P. Price, of this firm, worked out the process with great success, and were the first to produce this colouring matter in a pure state. The beautiful display of the crystallised acetate, shown at the Exhibition of 1862, illustrated this fully.

It was with products supplied by Mr Nicholson that Dr Hofmann made his first researches on this colouring matter. He changed its name from roseine to rosaniline, and found that the base, when in combination with acids, had the formula  $C_{20}H_{19}N_3$ .

The important observation of Nicholson, and the critical experiments of Hofmann, on the necessity of using, not pure aniline, but a mixture of aniline and toluidine for the production of this substance, was made about this period.<sup>1</sup>

The next important step in this industry was the use of rosaniline itself as a source of new colouring matters. For this we are indebted to the experiments of two French chemists, viz. MM. Girard and De Laire, who discovered that rosaniline salts, when heated with aniline, gave violet and blue colouring matters, which they called violet imperial and bleu de Lyon. It is, however, to Mr Nicholson that the credit of producing these bodies, in a practically pure state, belongs. This especially refers to the blue, the product known as opal blue, used by Dr Hofmann in his investigations on the subject, being of great purity. Dr Hofmann showed that these products were phenylated rosanilines, as is now well known, ammonia being given off

<sup>1</sup> In my original patent it was shown that colouring matters could be obtained not only from aniline, but also from toluidine, xyldine, and cumidine—these bases, as usually prepared at that date from the hydrocarbons obtained by fractioning coal-tar naphtha, not being pure, but mixtures.

in the reaction. And I may mention in passing that the manufacture of these blues is now carried on to such a large extent that the ammonia produced in this reaction is collected for the production of its sulphate or other salt.

One of the difficulties in the way of the new blue was its insolubility in water. Mr Nicholson, however (in 1862), probably thinking of the method used to render indigo soluble, experimented upon the action of sulphuric acid on this compound, and he found that it was possible to obtain sulphonic acids from it. One of these, the sodium salt of which is known as Nicholson's or alkali blue, is the monosulphonic acid, which is itself insoluble in water, but forms soluble salts, which can be applied to the goods, and then decomposed by acids. This compound has had much to do with the successful introduction of this colouring matter. The other product known as soluble blue is the sodium salt of the trisulphonic acid.

In the early part of 1864 the Hofmann violets were introduced. These, as is well known, are the ethylated rosanilines produced by acting upon rosaniline with ethyliodide. These colouring matters are more brilliant, though much more fugitive than mauveine; but by this time the desire for permanency was giving way very much to that of brilliancy; and these colouring matters were quickly taken up by dyers and calico printers.

About this time some colouring matters derived from phenol were introduced, and which, curiously, are found to belong to the class of substances now under consideration. These were brought forward by Messrs Guinon, Marnas & Bonnet, of Lyons. The first product was aurin, prepared from phenol by means of oxalic and sulphuric acid (Kolbe and Schmitt's process). The next was péonine, obtained by acting upon aurin with ammonia. The third was azuline, prepared by heating aurin with aniline. This last was a blue dye, which has since been shown to consist chiefly of triphenylrosaniline.

Purple and violet derivatives were also obtained from rosaniline by a process of my own, in which brominated turpentine was employed. These were known as Britannia violets, and were much used.

Other coloured derivatives were also discovered; for example, by the action of aldehyde and sulphuric acid, a blue product was obtained, which, when treated with sodium hyposulphite

or sulphuretted hydrogen water, yielded the well-known aldehyde green.

On examining the action of acetylchloride on Britannia violet, I obtained a peculiar green, which was used principally by calico printers, and very considerable quantities of acetylchloride were prepared for this purpose. The process was not published. This green was of a blue shade, and was obtained in a crystallised condition in combination with picric acid. The crystals had a golden metallic reflection.

Soon after this it was noticed that a green compound was produced in the preparation of the Hofmann violets, though generally only in small quantities. It was afterwards found that by making rosaniline react with an excess of methyl iodide it could be produced practically. It was called iodine green; but the product now manufactured is a chloride. This colouring matter gave good candlelight greens. One of its peculiarities is that when heated it is converted into violet methylrosaniline, with loss of methylchloride.

A new method of producing rosaniline violet was proposed by Lauth, and patented by MM. Porrier & Chappat, in June 1866. The process consisted in taking aniline, in which hydrogen had been replaced by an alcohol radical, and oxidising this instead of first preparing rosaniline, and then replacing the hydrogen in the colouring matter by the radical. The product proposed for this purpose was methylaniline.

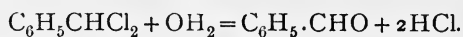
Owing to the improved method of methylating aniline, which, I believe, was first proposed by Messrs Girard and De Laire (*Bull. Chem. Soc.* [2], vii. 360), this process has become a very important one, and large quantities of dimethylaniline are now used, the oxidation being effected by copper salts. The product, according to the researches of Otto Fischer, consists chiefly of pentamethylpararosaniline.

The most important advance in the production of green colouring matters of the triphenylmethane series was the discovery of the benzaldehyde, Victoria, or malachite green.

In 1877, Otto Fischer, whilst investigating the condensation products of tertiary aromatic bases (*Ber.*, x. 1625), obtained by the action of benzaldehyde on dimethylaniline in presence of chloride of zinc, a colourless base of the formula  $C_{23}H_{26}N_2$ , the salts of which, when exposed to the air, rapidly oxidised to a fine blue-green dyestuff, which, he thought, would prove to be

of complicated constitution. A little later (*Ber.*, xi. 950) he showed that by treating this colourless base with some of the ordinary oxidising agents, this green could be more easily produced, and that it stood to the colourless compound in the same relation as rosaniline does to leucaniline. Emil and Otto Fischer afterwards said (*Ber.*, xii. 796) that the first experiments for the production of this green were made by the Badische Anilin- und Soda-Fabrik, in March 1878. About this time Oscar Doebner (*Ber.*, xi. 950) found that a green colouring matter was produced by heating benzaldehyde with benzoyltrichloride and zinc chloride. This product has been found to be identical with that of Fischer's. This green colouring matter is now largely made from benzaldehyde, as this process is found to be the best. A similar compound is also prepared from diethylaniline, and is known as brilliant green. It is a beautifully crystalline body. It is rather curious that this produces shades of colour somewhat yellower than the green from dimethylaniline, whereas, being of a higher molecular weight, we should have expected it to be bluer.

The principal difficulty which had to be contended with in the production of these colouring matters was the need of a supply of benzaldehyde. The usual method of obtaining it from bitter almonds, which was the only one in use, was quite out of the question, so that other sources had to be looked for. The Badische Anilin- und Soda-Fabrik, however, successfully overcame this difficulty. At first they experimented with the process of Lauth and Grimaux, which consists in the oxidation of benzylchloride, with an aqueous solution of lead nitrate; the product made by this process, however, was too dear. But they found that the decomposition of benzylidenedichloride, by means of water, as observed by Cahours (*Ann. Chem. Suppl.*, ii. 306) and Limpricht (*Ann. Chem.*, 139, 316), gave them a means of producing this compound practically, the reaction being as follows:



This process, which they have successfully employed since March 1878, consists in the preparation of benzylidenedichloride from pure toluene, and in the subsequent treatment of this chlorinated body with milk of lime, at 100° C.

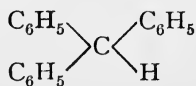
I have stated that the group of colouring matters under consideration are called triphenylmethane derivatives, and to

show how this has been proved to be the case, I must now refer very briefly to some of the theoretical work which has led to this knowledge. The most important of this refers to rosaniline. I have already drawn attention to the work of Hofmann, which gave us the first knowledge of the composition of this colouring matter, and the further information that it contained hydrogen, which could be displaced by phenyl and alcohol radicals; but as to the matter of constitution, I think the experiments of Caro and Wanklyn were the first, as they showed the relation which existed between rosaniline and aurin, or rosolic acid, and, in fact, they produced rosolic acid from rosaniline; but it is to the beautiful researches of Emil and Otto Fischer that we are indebted for a clear knowledge of the constitution of this class of colouring matter.

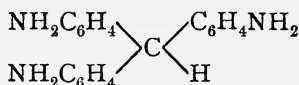
But to clear the ground before proceeding further, I must remind you that ordinary commercial rosaniline, or magenta, prepared from aniline and toluidines, is a mixture of colouring matters. This was first known to Mr Nicholson, who found that for the production of the finest blues it was necessary to purify the base and separate one of these before phenylating; but it is only of later years that the difference between these bodies has been carefully studied and explained. The base examined by Hofmann contained  $C_{20}$ , and is the chief constituent of commercial rosaniline. The other contains  $C_{19}$ , and is now called pararosaniline, because it is produced from aniline and paratoluidine. Similarly, in commercial aurin, two compounds are found, one containing  $C_{20}$ , now called rosolic acid, and one containing  $C_{19}$ , now called aurin; and these latter can be produced from the corresponding rosanilines; and Dale and Schorlemmer have shown that aurin can be also converted into pararosaniline by the action of ammonia (*Jour. Chem. Soc.*, xxxii. 121).

Emil and Otto Fischer, however, by submitting the leuco compound of commercial rosaniline to the diazo reaction, obtained the hydrocarbon  $C_{20}H_{18}$ , and from rosaniline prepared from paratoluidine and aniline the hydrocarbon  $C_{19}H_{16}$ .

And this latter hydrocarbon was found to be identical with Kekulé's triphenylmethane—



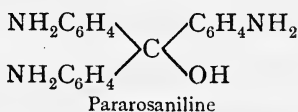
On nitrating this hydrocarbon, they obtained a trinitro derivative, which, when reduced, gave the triamido body,



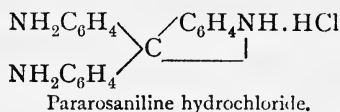
which is paraleucaniline, and by carefully heating its hydrochloride to  $150^\circ\text{--}160^\circ\text{C.}$ , it was converted into pararosaniline.

Also they found that by oxidising trinitrotriphenylmethane they obtained trinitrotriphenylcarbinol, and this when reduced gave pararosaniline direct.

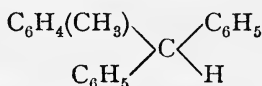
From these results the constitution of the base is evidently



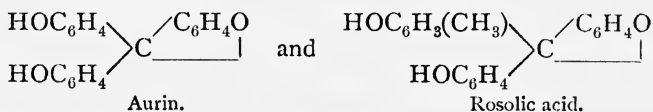
the salts—the hydrochloride, for example—being



Similar results were obtained from the hydrocarbon from rosaniline; it is tolyldiphenylmethane:

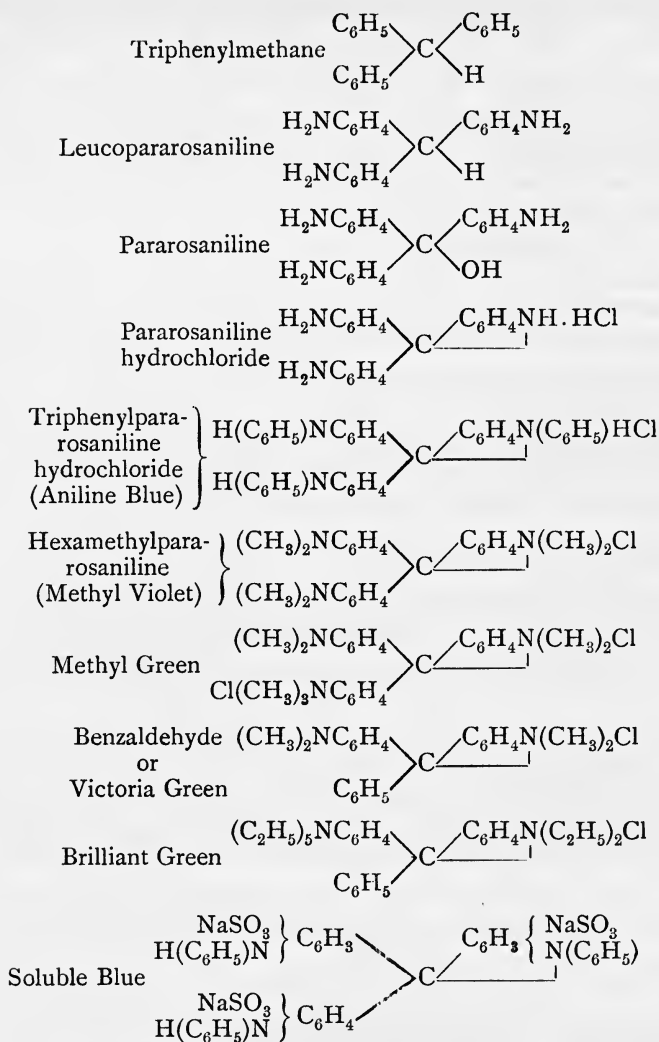


The rosolic acid and aurin corresponding to the rosanilines are constituted in an analogous manner:



From these results we see the beautiful relationships of the various colouring matters of this series to each other, and by it obtain information which is of practical value, as well as theoretical. The following formulæ of a few of these products further illustrate this:—





The effect of displacing hydrogen by hydrocarbon radicals in rosaniline is seen to result in the shade of colour becoming bluer for each hydrogen displaced—the effect of those of high molecular weight, such as phenyl, being to produce the greatest change; thus triphenylrosaniline is blue, whilst hexamethylrosaniline is blue violet, notwithstanding it contains six hydrogens displaced.

After all the displacements possible have been effected, as in hexamethylrosaniline, the result of the combination of the



products with halogen compounds of methyl is very interesting. The particular group to which this is attached becomes of the nature of an ammonium group, and the colour does not become bluer, but changes to green—*i.e.* methyl green,—and this, like other ammonium compounds, when heated, dissociates with loss of the halogen compound of methyl, and then hexamethylrosaniline is reproduced. Again, if this ammonium group be substituted by phenyl, we also get a green product—*i.e.* Victoria green.

The structure of some of these bodies has been proved by another most beautiful synthetical process, which has lately come into use—a process which enables us now not only to say that we employ the volatile products of the distillation of coal, but also the coke itself; as carbonic oxide in combination with chlorine (phosgene, or carbon oxychloride) is one of the important agents used. This substance was discovered in 1812 by J. Davy.

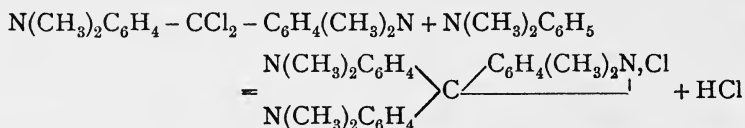
In 1876, W. Michler gave an account of his researches on the synthesis of aromatic ketones by means of phosgene (*Ber.*, ix. 716), in which he showed by the action of this substance on dimethylaniline that a tetramethylated diamidobenzophenone was obtained. This substance has, therefore, the constitution



The formation of this product takes place in two phases, but I need not enter into that now.

The first experiments to turn Michler's synthetically prepared tetramethylated diamidobenzophenone to practical account were made by Dr A. Kern, in the works of Bindschedler, at Basle. Dr Kern proved that an agent like phosgene might be produced on a larger scale, and he invented a process to convert Michler's ketone base into methyl purple. This process was derived from the ketone synthesis of triphenylmethane from benzhydrol and benzene, and consisted in preparing the tetramethyldiamidobenzhydrol, and condensing the latter with dimethylaniline; thus the leuco base of hexamethylrosaniline was obtained, and then oxidised with lead peroxide. This process, which was too costly for practical purposes, has been superseded by one discovered by Dr Caro, who has found that this ketone base can be made to form condensation products with dimethylaniline and other products directly, by the use of phosphorus tri-

chloride—this substance converting it first into a chloride, which then reacts on the dimethylaniline, thus—



And this reaction takes place quantitatively, the body being so pure that it readily crystallises from water in prisms, like potassium permanganate, only with a very much more brilliant lustre. These contain water of crystallisation. The condensation can also be effected with phosgene gas. The colouring matter obtained by this means is bluer than that obtained from dimethylaniline by oxidation, which consists chiefly of the pentamethyl compound.<sup>1</sup>

Diethylene can also be made into a ketone with phosgene or carbon oxychloride, and this product condensed with diethylaniline yields hexaethylpararosaniline.

Instead of dimethylaniline, dimethyl- $\alpha$ -naphthylamine can be used, and in this case a beautiful blue colouring matter is obtained, and if  $\alpha$ -phenylnaphthylamine be employed, the Victoria blue is produced, and by varying the reaction in this kind of way a great variety of colouring matter can be synthetically prepared.

With ammonia this ketone condenses to form the new yellow colouring matter, auramine, with aniline phenylauramine. With quinoline it produces a green very similar to Victoria or benzaldehyde green. I must not, however, spend any more time over this interesting part of the subject, but may say here again we have pure scientific research conducted for its own sake, bearing fruit. The discovery of W. Michler, which remained for seven years a matter of theoretical interest, now comes forward as a matter of practical value.

#### ANTHRAQUINONE SERIES

I must now draw your attention to the important class of colouring matter compounds obtained from anthracene or anthraquinone.

<sup>1</sup> See Caro, Eng. Patents, 4428, September 1883; 4850, 13th March 1884; and 5038, 18th March 1884.

Alizarin and the other colouring matters related to it form one of the most important branches of the coal-tar colour industry, and one of special interest, because alizarin was the first instance of the production of a natural colouring matter artificially. It will be quite unnecessary for me here to say much about the madder-root, which was the original source of alizarin, and was grown in such enormous quantities, but now is nearly a thing of the past ; nor will I enter into the early chemical history of alizarin, and all the laborious work which was bestowed upon it by Dr Schunck and others. As you are probably all aware, the relationship of alizarin and its formation from the coal-tar hydrocarbon anthracene was the result of the labours of Graebe and Liebermann, the researches which culminated in this being of a purely scientific nature. The original process for obtaining it has, however, not been found of practical value, but a new one in which sulphuric acid could be used in place of bromine was afterwards discovered by Caro, Graebe and Liebermann in Germany, and by myself in this country, apparently simultaneously. A second process was also discovered by me which was worked nearly all the time I was engaged in this industry. In this, dichloranthracene was used instead of anthraquinone, and the product thus obtained yielded colours of a brilliancy which it has been found, even to the present time, difficult to match by the anthraquinone process.

At the time of the discovery of artificial alizarin, anthracene was not prepared by the tar distillers, as it had no application, and very little was known about it. It was discovered in 1832 by Dumas and Laurent. In 1854-55, when studying under Dr Hofmann, I worked with it for some time, but my results were never published, because, owing to the erroneous formula given to it by Dumas and Laurent, which was accepted, my results would not fit in ; nevertheless the information obtained afterwards proved of great value to me, although at the time the labour spent appeared to be lost labour, showing the value of research even when not successful. The formula of this hydrocarbon was not established until 1862, when it was studied by Dr Anderson. This was only six years before the discovery of Graebe and Liebermann, and, had not the formula of anthracene been established before these chemists commenced their work, the relationship of alizarin to it would not have been discovered, and up to this day it is possible that this

artificial alizarin industry would not have been in existence. Researches like that of Dr Anderson I have often heard spoken of slightly, because they don't bear much on their surface; but who knows what such work may lead to? Earnest workers cannot be too much encouraged.

As anthracene was not a commercial product, it was necessary to experiment on its production before alizarin could be manufactured, and not only on the best methods of getting it, but also to get a rough idea of how much could be produced, because unless the hydrocarbon could be obtained in large quantities, artificial alizarin could not compete with madder. In our works at Greenford Green we commenced by distilling pitch; but afterwards tar distillers were induced to try to separate it from the last runnings of their stills by cooling and then filtering off the crystalline products which separated out, and in fact visits were paid to most of the tar distillers of the United Kingdom, others being corresponded with on the subject, and the result was that in a short time such quantities came in that the distillation of pitch was abandoned. And although much doubt and anxiety prevailed at first as to the possibility of getting a sufficient supply of this raw material, two or three years since there were about 1000 tons of commercial anthracene (about 30 per cent.) produced in excess of the requirements, the annual production in the United Kingdom being estimated at about 6000 tons 30 per cent., or nearly 2000 tons pure anthracene.

Although the colouring matter obtained from anthraquinone or dichloranthracene was at first simply considered as alizarin more or less pure, yet on investigating the matter it was soon found that it contained other colouring matter. To this I drew attention in 1870 (*Jour. Chem. Soc.*, xxiii. 143, footnote), and in 1872 gave the analysis of a product which I named anthrapurpurin, followed by a more extended account a year afterwards (*Jour. Chem. Soc.*, xxv. 659, and xxvi. 425). It was called anthrapurpurin because it is an anthracene derivative having the formula of purpurin, with which it is isomeric. In the latter paper I also referred to another colouring matter dyeing alumina mordants of an orange colour (*Jour. Chem. Soc.*, xxvi. 425). It was also shown that anthraflavic acid when fused with alkali gave a colouring matter behaving with mordants in the same way (*Jour. Chem. Soc.*, xxvi. 20) and this has proved to be the

same body. This latter reaction was afterwards more fully studied by Schunck and Roemer, and the colouring matter produced by it was shown also to have the formula of purpurin; they therefore called it flavopurpurin (*Ber.*, ix. 678), so that the colouring matters formed have proved to be three in number—alizarin, anthrapurpurin, and flavopurpurin, all of which are valuable dyes, whereas in madder-root there is only alizarin and purpurin, the latter being of but secondary value. This can now also be produced from anthracene. The researches which have been made on the subject of the conditions under which these different colouring matters are formed, have led to the discovery of methods for their separate production, so that in artificial alizarin, which name commercially embraces all these colouring matters, both mixed and separate, we have more than a simple replacer of madder-root, and as these colouring matters just referred to can be applied with the same mordants, varieties of styles of work can be produced by the calico printer and dyer which before were unknown. Anthrapurpurin is, I believe, of as great importance as alizarin itself, and used with it increases its brilliancy, and alone gives very brilliant scarlet shades.

Artificial alizarin was first produced commercially in this country by my firm at Greenford Green in 1869, when 1 ton was produced; in 1870, 40 tons were made; in 1871, 220 tons, and so on increasingly. It was not produced on the Continent until 1871, when, according to Graebe and Liebermann, 125–150 tons were made. These weights do not apply to dry colour, but to paste.

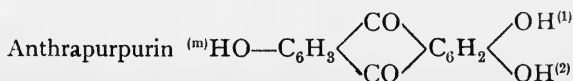
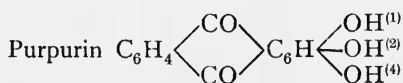
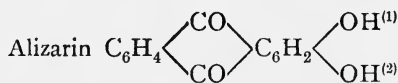
I cannot go into any lengthened account of the chemistry of this industry here; its development, however, has kept pace with theoretical investigations, in some cases it may be said to have forestalled it. For example, in the old methods of working, more anthrapurpurin than alizarin was produced; the conditions required to modify this were found out by experiment. According to all our previous knowledge as to the introduction of hydroxyl into a body by the fusion of its sulphonic acid with alkali, a monosulphonic acid should give a monohydroxyl compound, and a disulphonic acid a dihydroxyl compound. Therefore to produce alizarin, which is a dihydroxyl compound, an anthraquinone disulphonic acid was thought to be the proper thing to use. By experience this was gradually found to be

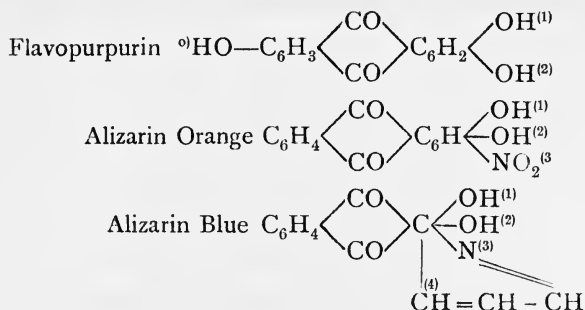
incorrect, a monosulphonic acid being required to produce alizarin, a disulphonic giving anthra or flavopurpurin, the colouring matter not being due to the primary but to a secondary reaction, as was afterwards shown by research—the mono and dioxyanthraquinones (the latter known as anthraflavic and isoanthraflavic acids) being the first products of the reaction, and then undergoing oxidation by the caustic alkali employed, yielding the corresponding colouring matter, a portion of the products, however, being at the same time reduced back to anthraquinone.

A very important improvement preventing this loss by reduction was discovered by J. J. Koch, who found it might be avoided by the use of a small quantity of potassium chlorate with the alkali used in the fusion.

The amount of caustic soda used in this industry is very large, and at the Badische Anilin- und Soda-Fabrik—and, I believe, elsewhere—it is made on the spot; and I must say the cleanly way in which alkali is made in the above works contrasts very favourably with what I have seen in some of the alkali works in this country.

Like rosaniline, alizarin has now become a material for preparing other colouring matters. Of these there are two in use—viz. nitroalizarin, which gives orange-yellow shades with alumina mordants, and alizarin blue, a remarkable compound prepared from nitroalizarin by treating it with sulphuric acid and glycerol. This gives shades of colour like indigo. When first discovered, considerable difficulty was found in its application on account of its insolubility; it has since been found to form a soluble compound with sodium bisulphite, and by this means its application has become much easier. The constitution of the colouring matter derived from anthracene may be represented as follows :—





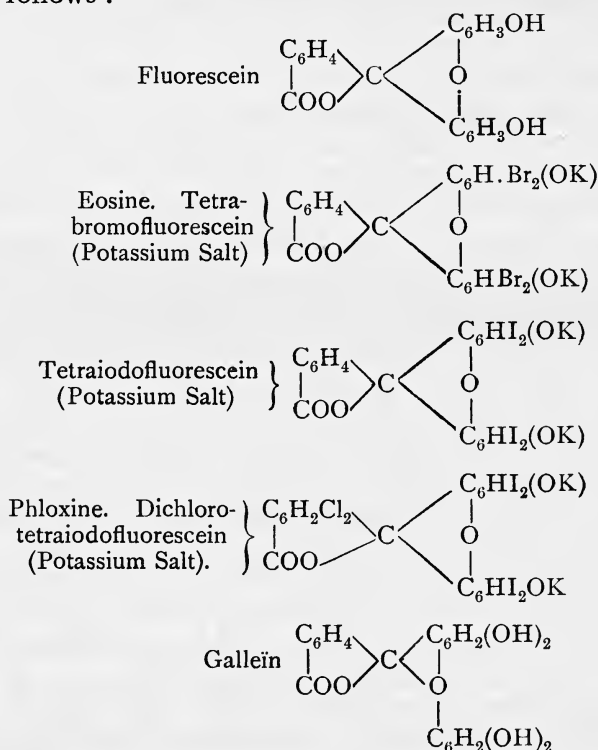
Those colouring matters under the name of artificial alizarin are the most important of the coal-tar colours, their money value amounting to more than a third of the entire value of all the colours produced in this industry, and at present the price of artificial alizarin compared tinctorially is not more than one-fourth of that of madder or garancine before their production. There are now three works producing it in this country, but the bulk of that used still comes from Germany.

### PHTHALEINES

The discovery of this class of bodies dates back to 1871, and was the result of the investigation of Baeyer. He found that phenols unite with a number of polybasic acids and with aldehydes, with separation of water when the mixture is heated alone, or with glycerol and sulphuric acid, the compounds formed not being ethers. Those produced when phthalic anhydride is employed, and which embrace those of practical value, are called phthaleines. The first of these discovered by Baeyer was galleïn (*Ber.*, iv. 457), produced by heating pyrogallol with phthalic anhydride; its formula is  $\text{C}_{20}\text{H}_{14}\text{O}_5$ ; by reduction it loses the elements of water and combines with hydrogen, forming cœruleïn. These colouring matters, which for a long time remained unnoticed, are now being extensively used.

Later, in 1871, Baeyer discovered resophthaleïn, or fluoresceïn (*Ber.*, iv. 555). This substance, which is remarkable for its yellowish-green fluorescence, dyes silk and wool yellow, but does not combine with mordants, and is not a very useful dyeing agent. But it was discovered by Caro in 1874, the subject being afterwards worked out jointly with Baeyer, that fluoresceïn when brominated yielded that beautiful dyestuff now called eosine;

this was introduced into the market in July 1874. Other substitution products were then studied, and the iodine product was found to give bluer shades of red than the bromine derivative. One of the most beautiful colours of this series is the dichlorotetraiodofluorescein, in the preparation of which dichlorophthalic anhydride is used. It is called phloxine. The methylic ether of eosine and its nitro derivative also have become commercial articles. These bodies are now manufactured in a practically pure condition. Their structure has been made out by research to be as follows :—



The introduction of these colouring matters had a great influence on the manufacture of phthalic acid. This acid, it will be remembered, was proposed a good many years since as a source for the production of benzoic acid, which was largely in demand for the manufacture of aniline blues, phthalic acid when carefully treated with lime yielding calcium benzoate. But as phthalic acid was required to be produced in an extensive way, new experi-



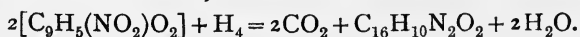
ments had to be made on the subject. The difficulties connected with this were surmounted by the Badische Anilin- und Soda-Fabrik, who are now the chief manufacturers of this body and its anhydride, which is the substance required ; when freshly prepared it is one of the most beautiful products one can see.

Phthalic anhydride and dichlorophthalic acid are now also manufactured for the preparation of the bluish shades of fluorescein derivatives already referred to. But this is not all ; it was not only necessary to produce these in quantity, but it was necessary also to produce resorcinol. This substance was originally prepared from certain resins, *e.g.* galbanum by fusing it with potash, or by distilling brazilin, etc. ; both technically impractical processes. It was afterwards produced by fusing various halogen derivatives of phenol and benzene sulphonic acid with alkali ; these also were not practical processes. It was, however, eventually found that it could be produced by fusing metabenzenedisulphonic acid with potash, the original observation being made by Gallik ; and by this process this product, which was a rare compound, is now manufactured and has become a common one, being produced in very large quantities.

#### INDIGO SERIES

Indigo is too well known a substance for me to make any remarks in reference to its history as a colouring matter, and with reference to the chemical side of the question I suppose few substances have had more work bestowed upon them than this body, so that I must confine my few remarks to its artificial formation. There is one point of interest, however, connected with indigo, and that is that it was the original source of aniline, this base being discovered in the products of its destructive distillation by Unverdorben, in 1826, as already mentioned.

Notwithstanding the large amount of work which has been bestowed upon this colouring matter, its constitution has only been lately arrived at, and for this, and the methods of its artificial formation, we are indebted to the beautiful and laborious researches of Baeyer. The first process for its artificial production was patented by Baeyer in March 1880. The process consists in preparing orthonitropropionic acid and acting upon it in presence of an alkali, with a reducing agent, such as grape sugar, xanthate of sodium, etc. :

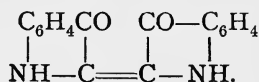


This process renders the application of artificial indigo very easy in calico printing, because the products can be applied to the fabric and the reaction then completed, and thus the indigo is formed and fixed in the fibre ; and this process is in use in some of the print-works of Mulhouse, where there is a continued though small demand for orthonitropropionic acid. Other processes have been discovered by Baeyer for the formation of indigo ; he has found that it can easily be formed from ortho-nitrobenzaldehyde by condensation with bodies containing the  $\text{CH}_3\text{CO}$  group, such as acetone.

Hitherto this artificial formation of indigo has not met with much practical success. This does not arise from difficulties in its manufacture, but in its cost compared with natural indigo, which is a very cheap dyestuff.

So far as it has been manufactured, however, the possibility of this has been entirely dependent upon scientific research disconnected with its study. To prepare nitropropionic acid it is necessary to begin with cinnamic acid as a raw material. This acid, until 1877, was only obtained from certain balsams, and was a very costly material. It was then discovered that it could be produced with comparative ease by the action of acetic anhydride and an acetate on benzaldehyde (*Jour. Chem. Soc.*, xxxi. 428). Caro afterwards found that this process might be simplified by heating a mixture of benzylidene dichloride with sodium acetate, and it is by this process that it is now prepared.

The constitution of indigo Baeyer represents as follows :—



Several derivatives have been made which are interesting dyes, such as methyl indigo, tetrachlor indigo, etc.

### Azo COMPOUNDS

The commencement of the history of the azo colours in an industrial sense has little to do with the theoretical side of the question, the early products being the offspring of empirical observations, and in no way connected with the theory of the diazo compounds, a condition of things very different from that now existing. Time will not allow me to enter into the beautiful

work of Griess, much of which will be found in the *Philosophical Transactions* for 1864.

The first definite compound of this class, shown to possess dyeing powers, was a substance discovered by Prof. Church and myself, known first as nitrosonaphthalene, then as azodinaphthyl-diamine, but now called amidoazonaphthalene. This substance, however, was of no practical value, because its salts, which are violet, cannot exist except in the presence of a certain amount of free acid. This substance has since been found of value in the preparation of the Magdala red.

The first substance of this class sent into the market was the phenylic analogue of amidoazonaphthalene — viz. amidoazobenzene, which was discovered by Mène. It was introduced by Nicholson, who prepared it by a process which has not been published. It was afterwards patented by Dale and Caro in 1863. It is a yellow dye, but did not command success, because of its volatility. It has, however, since become useful for the manufacture of induline.

The first really successful azo colour was Manchester or Bismarck brown (triamidoazobenzene), which is produced by the action of nitrous acid on metadiamidobenzene.

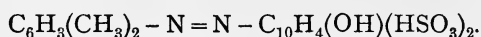
The next important step took place in 1876, by the discovery of chrysoidine, by Caro and Witt. Independently, this product is prepared by the action of diazobenzene on metadiamidobenzene.

About this time the subject began to be worked out on a scientific basis, and since then the number of diazo dyes produced is marvellous, and it will be useless for me to do more than refer to one or two of the most important. About this period also the value of the sulpho group began to be realised, and this has greatly added to the value of these dyes.

The first use of the sulpho group in relation to azo colours was in connection with amidoazonaphthalene, patented by myself in 1863.

During the early history of the coal-tar colours, innumerable experiments were made with naphthalene derivatives to produce colouring matters, but no results of any value were obtained; the experiments were mostly made with naphthylamine. The first colouring matter that was obtained from it that was of value was Martius's yellow, a dinitronaphthol. After this came the Magdala red, which was not much used. The principal development of the coal-tar colours of late years has, however, been in

connection with diazo reaction. In these reactions  $\beta$ -naphthol is much used, and this product, which a few years ago was unknown, is now manufactured by tons by fusing naphthalene sulphonic acid with alkali, and is produced at a few pence per pound. Most of the azo colours produced from benzene derivatives are of a yellow or brown colour, but, by taking products of a higher molecular weight, colours of different shades of red are produced. The one which has commanded the greatest success is the scarlet, first known as Meister's scarlet, produced by the action of diazoxylene chloride on the disulphonic acid of  $\beta$ -naphthol; its constitution may be represented thus :



In the formation of bluer shades, diazocumene chloride is used. The cumidine used is now made from xylidene, by the beautiful reaction of Hofmann's, in which an alcohol radical associated with the nitrogen leaves that element, and enters into the hydrocarbon radical. These scarlets have had a very injurious influence on the cochineal market, and have in many cases displaced cochineal.

If  $\alpha$ -diazonaphthalene chloride be used instead of the xylene or cumene compounds, the colours known as Bordeaux are produced. Then, again, where derivatives of  $\alpha$ -naphthol are used, different results are also obtained, so that great varieties of products can be produced. The preparation of these azo colours is a matter of great simplicity, the colouring matter being precipitated by bringing the products together, and, moreover, they can be produced in almost theoretical yields; hence they are remarkably cheap dyeing agents. The following are the formulæ of some of these azo dyes :—

Bismarck Brown.  $\text{NH}_2\text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2\text{HCl}.$

Chrysoidine.  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2\text{HCl}.$

Fast Yellow.  $\text{KSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{NH}_2.$

Manchester Yellow.  $\text{NaSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{NHC}_6\text{H}_5.$

Orange.  $\text{NaSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6(\text{OH})^\beta.$

Fast Red.  $\text{NaSO}_3 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6(\text{OH})^\beta.$

Ponceau G.  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_4\text{OH}(\text{NaSO}_3)_2^\beta.$

Ponceau 2R.  $(\text{CH}_3)_2\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_4\text{OH}(\text{NaSO}_3)_2^\beta.$

Bordeau.  $\text{C}_{10}\text{H}_7 \cdot \text{N}_2^\alpha \cdot \text{C}_{10}\text{H}_4\text{OH}(\text{NaSO}_3)_2^\beta.$

From which it will be seen that the colour changes from yellow to red and claret by the increase of the molecular weight of the radicals introduced, and also by the relative position occupied by the groups, etc.

### QUINOLINE COMPOUNDS

Products of the quinoline series have of late been claiming attention in relation to colouring matters. It will perhaps be remembered that, in the early days of the coal-tar colour industry, a beautiful blue colour belonging to this series, discovered by Greville Williams (*Chem. News*, 11th Oct. 1860, 219), was introduced. This substance was called cyanine. Its employment as a dye for silk at first produced quite a sensation, on account of the beauty of the colour; but unfortunately it was too fugitive to be of any practical value. Recent researches have shown that chrysaniline is also to be regarded as a body of the quinoline class. Alizarin blue, and the beautiful yellow dye obtained from acetanilide by Fischer, and known as flavaniline, are found also to belong to this class of substances.

Other colouring matters which have since been prepared from quinoline direct might be referred to did time permit. The peculiar green which is produced by the condensation of tetramethyldiphenylketone with quinoline is of interest, because the introduction of this quinoline has a very different influence on the resulting colouring matter from that of groups containing amidogen—in fact, it appears to act more like phenyl, as the green is very analogous to benzaldehyde green.

There is a very interesting new manufacture growing out of the coal-tar colour industry, and that is the preparation of derivatives of quinoline as substitutes for quinine. I have mentioned that much work has of late been directed to the study of quinine itself, and although the artificial formation of this substance has not yet been discovered, new bodies have been obtained during these investigations which are thought to possess valuable medicinal properties. This is rather a remarkable development from this industry, seeing that it is owing to experiments made on the artificial formation of quinine that it owes its foundation.

There is another peculiar colouring matter I have not yet referred to—peculiar, as it contains sulphur. I refer to methylene blue, a very valuable dye, the constitution of which

has been so well worked out by Bernthsen. I feel I must be content with this slight reference to it.

As I have shown, the coal-tar colour industry originated in this country, where for some time it was solely carried on. The second impulse was from France in the discovery of magenta and its blue and purple phenyl derivatives, which were soon brought to a state of great purity in this country. The Hofmann violets were then discovered and produced also in this country, several other colours being perfected and largely used. By this time the manufacture of coal-tar colouring matter had made some progress in Germany and Switzerland; crude products in a cheap form were first made, but improvements soon followed. The subject of these colouring matters was taken up with great earnestness in the German laboratories, so much so that it was stated at one time that this industry was acting injuriously to science, as it had diverted an undue amount of attention from other subjects. Time has, however, proved the groundlessness of this statement. This laboratory work, as well as research work generally, fitted a number of highly trained chemists to enter the colour works, where they soon improved the processes, and thus they were able to produce products of a quality to compete with those of English manufacture, which had, owing to their purity, given superior and more reliable shades of colour in the hands of the dyer; and the result of the application of such scientific labour to this industry is that Germany produces products of the highest class and at the lowest price. The fact that Germany is now the headquarters of this industry, raises the important question, Why has England allowed this state of things to come about? All the raw materials are produced in this country, both the products from coal and the other chemicals required, and, as we have seen, the industry originated and was first carried on here, and, in addition, we are the greatest consumers of the colouring matters. This fact is well worth considering, and it is many-sided. In my opinion, the patent laws, and the difficulty of preventing infringements from abroad, was one cause which may have prevented this country from maintaining its first position.

When speaking of the early history of the first coal-tar colour mauveine, I referred to this class of infringement and how it was first met by the proceedings taken against the agents employed in this country, and that this course was so far successful, but

only pointed out how easily the law could be evaded if foreign manufacturers gave up responsible agents and sold direct to the consumers. There being no duties on such articles, no assistance could be obtained at the Customs, and the colouring matters were generally declared under the name of vegetable dyes or extracts, so that it was impossible to stop them entering the country, and even when found, owing to the onus of proof of their being manufactured by the patentee's process resting with the patentee, an almost insurmountable difficulty was raised, as in most cases no traces of the products used in the preparation were left in the colouring matter. The only other proceedings which could be instituted were against the consumer ; here again the difficulties were practically insuperable.

In most cases the consumers were using the patentee's products to some extent, and it was impossible to know to what extent ; in fact, without going into the many details connected with this point, it may be assumed that in most cases proceeding against a consumer of this kind of article is practically useless.

The result of this infringement, by importation from abroad, is that a patentee had to compete against all other manufacturers with the exception of his own countrymen.

There can be but little doubt that this state of things has had much to do with preventing the development of this industry, and crippling enterprise in this country, as it prevented manufacturers even from working under royalties, there being no security whatever except in name. Again, the fact that a foreigner could take a patent in this country, manufacture in his own country, and send the product here, was a great source of loss and mischief to our trade. The new patent laws may probably alter this, but still the difficulty of importation in defiance of patent rights still remains.

There is another matter which tells much against this country—namely, that we are not able to export colour to foreign countries upon the same conditions as foreign manufacturers can into this, because we are met with import duties which handicap us to a prohibitive extent, whereas the foreign manufacturer, being protected in his own country, may maintain his prices there and sell at a lower price in this country ; but what is still more injurious, he may dispose of surplus production in this country at or even below cost price. The injurious effect of such a course upon our market can be easily understood by business

men, and I need not go into it here. These are matters our manufacturers have to contend with, and cannot help themselves ; there is, however, one matter in which they are undoubtedly at fault.

We find that in Germany the manufacturer understands the value of well-trained chemists, and sympathises with them ; they also realise the value of theoretical chemistry—this is a condition of things we don't find in this country.

Unless I am mistaken, the coal-tar colour industry has acted as the great stimulus to the development of general chemical industries of Germany, and these, by starting with so much scientific aid as they have called to their assistance, have made an amount of progress during the last twenty-five years which is most remarkable. Up to that time England had been the seat of most of the large chemical industries, and the success which we have had appears to me to have produced a feeling of false security, and more attention has been paid by the heads of firms to the markets than to the chemistry of their manufactures.

I believe that thirty years ago there were very few chemists employed in chemical works, either in this country or on the Continent. Now there are very few without them ; but in this country they are far less numerous and much less efficient than in Germany, and for this our manufacturers are to a great extent responsible. I am told that at some of our large chemical centres, the chemists, or so-called chemists, are sometimes paid not more than could be earned by a bricklayer. If such openings are put by manufacturers before young men, their parents are not likely to give them an expensive scientific training. If they get any, they are not likely to continue it longer than enough to do analysis very imperfectly, say by studying for about nine months. An ordinary tradesman would not be considered efficient unless he passed a much larger apprenticeship than this, but I know teachers complain that it is difficult to get students who are to be works chemists to stay longer than this. The result is that when really efficient men are wanted, they are not to be found, and they have to be got from abroad. In my address to the Chemical Society last year, I referred to the past neglect of research at our chemical schools, so that I need not speak further on that aspect of the subject here, though it is an important one in relation to our industries.

There is no chasm, as we have already seen, between pure



and applied chemistry, they do not even stand side by side, but are linked together, so that a technical chemist needs to be a thorough chemist, and unless we employ such men we must be at a great disadvantage in relation to foreign manufacturers.

I have now given a very brief, and therefore a very imperfect, outline of the history of the coal-tar colour industry, an industry to which none other can be compared for its rapid progress. I have drawn your attention to the fact that it is the offspring of scientific research, that in return, as I before stated, it has in many cases given a fresh impulse to research by giving the chemist new products, and also by opening up new subjects of theoretical interest for consideration, and from the fruits thus resulting again reaping further benefit. This linking together of industrial and theoretical chemistry has undoubtedly been the great cause of its wonderful development. We now have not only all the colours of the rainbow, but we have also the more sombre, but often not less useful, colours, and, moreover, there are also great varieties of products of similar colour possessing different properties which fit them for special uses. This industry is also one of no mean dimensions. I have not been able to get any very recent statistical information on this subject, but notwithstanding the great reduction of prices of the products of late years, yet, owing to the extended development it has undergone, the value of the annual output has probably increased and not declined, and from what information I have on the subject I should say it is perhaps not less than £3,500,000.

In my remarks I have also been led to refer to some of the points connected with the migration of this industry from this country to Germany, and the probable influence our patent laws had upon this, to the matter of technical education, and the employment of high-class chemists in chemical works. This latter subject is undoubtedly of great importance, and requires the earnest consideration of our manufacturers. If it is found profitable to employ chemists of this class on the Continent, surely it should be found equally profitable to employ them here. In conclusion, I am happy to say there are signs of the coal-tar colour industry returning to our country, in part at any rate, especially in relation to alizarin, for which there are now three large works in existence, and the production of other colouring matters is also increasing.

VII.: 1886

## RECENT PROGRESS IN THE COAL-TAR INDUSTRY

BY PROFESSOR SIR H. E. ROSCOE, M.P., LL.D., F.R.S.

(Discourse delivered at the Royal Institution, 16th April 1886)

THOSE who have read Goethe's episodes from his life, known as *Dichtung und Wahrheit*, will remember his description of his visit in 1741 to the burning hill near Dutweiler, a village in the Palatinate. Here he met old Stauf, a coal philosopher, *philosophus per ignem*, whose peculiar appearance and more peculiar mode of life, Goethe remarks upon. He was engaged in an unsavoury process of collecting the oils, resin, and tar, obtained in the destructive distillation of coal carried on in a rude form of coke oven. Nor were his labours crowned with pecuniary success, for he complained that he wished to turn the oil and resin into account, and save the soot, on which Goethe adds that in attempting to do too much, the enterprise altogether failed. We can scarcely imagine, however, what Goethe's feelings would have been could he have foreseen the beautiful and useful products which the development of the science of a century and a half has been able to extract from Stauf's evil-smelling oils. With what wonder would he have regarded the synthetic power of modern chemistry, if he could have learnt that not only the brightest, the most varied colours of every tone and shade can be obtained from this coal tar, but that some of the finest perfumes can, by the skill of the chemist, be extracted from it. Nay, that from these apparently useless oils, medicines which vie in potency with the rare vegeto-alkaloids can be obtained, and lastly, perhaps most remarkable of all, that the same raw material may be made to yield an innocuous principle, termed saccharine, possessed of

far greater sweetness than sugar itself. The attainment of such results might well be regarded as savouring of the chimerical dreams of the alchemist, rather than expressions of sober truth, and the modern chemist may ask a riddle more paradoxical than that of Samson, "Out of the burning came forth coolness, and out of the strong came forth sweetness"; and by no one could the answer be given who had not ploughed with the heifer of science, "What smells stronger than tar and what tastes sweeter than saccharine?" That these are matters of fact we may assure ourselves by the most convincing of all proofs—their money value,—and we learn that the annual value of the products now extracted from an unsightly and apparently worthless material, amounts to several millions sterling, whilst the industries based upon these results give employment to thousands of men.

#### SOURCES OF THE COAL-TAR PRODUCTS

In order to obtain these products, whether colours, perfumes, antipyretic medicines, or sweet principle, a certain class of raw material is needed, for it is as impossible to get nutriment from a stone as to procure these products from wrong sources. All organic compounds can be traced back to certain hydrocarbons, which may be said to form the skeletons of the compounds, and these hydrocarbons are divisible into two great classes: (1) the paraffinoid, and (2) the benzenoid hydrocarbons. The chemical differences both in properties and constitution between these two series are well marked. One is the foundation of the fats, whilst the other class gives rise to the essences or aromatic bodies. Now all the colours, finer perfumes, and antipyretic medicines referred to, are members of the latter of these two classes. Hence if we wish to construct these complicated structures, we must employ building materials which are capable of being cemented into a coherent edifice, and therefore we must start with hydrocarbons belonging to the benzenoid series, as any attempt to build up the colours directly from paraffin compounds would prove impracticable. Of all the sources of hydrocarbons, by far the largest is the natural petroleum oils. But these consist almost entirely of paraffins, and hence this source is commercially inapplicable for the production of colours. We have, however, in coal itself, a raw material which by suitable treatment may be made to yield oils of a valuable character. Of these treatments,

that followed out in the process of gas-making is the most important, for in addition to illuminating gas in abundant supply, tar is produced which contains principally that benzenoid class of substances already referred to, and which, to use the words of Hofmann, "is one of the most wonderful productions in the whole range of chemistry." The production of these latter as distinguished from the paraffinoid group appears to depend upon a high temperature being employed, to effect the necessary decomposition.

The quantity of coal made into coke for use in the blast furnace is larger than that distilled for gas-making, no less than between eleven and twelve million tons of coal being annually consumed in the blast furnaces of this country in the form of coke, and being capable of yielding two million tons of volatile products. Up to recent times, however, the whole of these volatile products has been burnt and lost in the coke ovens. But lately, various processes have been devised for preventing this loss, and for obtaining the oils, which might be made available as colour-producing materials. It is, moreover, a somewhat remarkable fact that only in one or two cases have the conditions been complied with which render it possible to obtain the necessary benzenoid substances. In the ordinary coking ovens, as well as in the blast furnaces, although the temperature ultimately reached is far in excess of that needed to form the colour-giving hydrocarbons, yet the heating process is carried on so gradually that the volatile products from the coal are obtained in the form of paraffinoid bodies mainly, and hence are useless for colour-making purposes. Amongst the few coking processes in which the heat is suddenly applied, and consequently a yield of colour-giving hydrocarbons is obtained, may be mentioned the patented process of Simon-Carvès, the use of which is now spreading in England and abroad. The tar obtained in this process is almost identical in composition with the average gas-works tar, whilst the coke also appears to be equal for iron-smelting purposes to that derived from other coke-ovens. A third source of these oils yet remains to be mentioned, viz. those obtained as a by-product in blast furnaces fed with coal.

Another condition has, in addition, to be considered in this industry, and that is the nature of the coal employed for distillation. It is a well-known fact that if Lancashire cannel be exclusively employed in gas-making a highly luminous gas is

obtained, but the tar is too rich in paraffins to be a source of profit to the tar-distiller, whilst, on the other hand, coal of a more anthracitic character, like that from Newcastle or Staffordshire, yields a tar too rich in one constituent, viz. naphthalene, and too poor in another, viz. benzene. It is also known to those engaged in carbonising coal principally for the sake of the tar that the coal from different measures, even in the same pit, yields tars of very different constitution. That under these varying conditions products of varying composition are obtained is a result that will surprise no one who considers the complicated chemical changes brought about in the process of the destructive distillation of coal.

### HISTORY OF BENZENE AND ITS DERIVATIVES

Having thus sketched the principles upon which the formation of these valuable tar colours depends, we should do wrong to pass over the history of the discovery of benzene ( $C_6H_6$ ), which contributed so much to the unlocking of the coal-tar treasury.

Faraday in 1825 discovered two new hydrocarbons in the oils obtained from portable gas. One of these was found to be butylene ( $C_4H_8$ ); to the other Faraday gave the name of bicarburet of hydrogen, as he ascertained its empirical formula to be  $C_2H$  ( $C=6$ ). By exploding its vapour with oxygen, he observed that one volume contains 36 parts by weight of carbon to 3 parts by weight of hydrogen, and its specific gravity compared with hydrogen is therefore 39.<sup>1</sup>

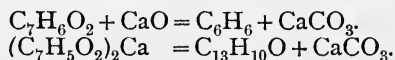
Mitscherlich, in 1834, obtained the same hydrocarbon by distillation of benzoic acid,  $C_7H_6O_2$ , with slaked lime, and termed it benzin. He assumed that it is formed from benzoic acid simply by removal of carbon dioxide. Liebig denied this, adding the following editorial note to Mitscherlich's memoir:—"We have changed the name of the body obtained by Professor Mitscherlich by the dry distillation of benzoic acid and lime, and termed by him benzin, into benzol, because the termination 'in' appears to denote an analogy between strychnine, quinine, etc., bodies to which it does not bear the slightest resemblance, whilst the ending in 'ol' corresponds better to its properties and mode of production. It would have been perhaps better if

<sup>1</sup> *Phil. Trans.*, 1825, p. 440.

the name which the discoverer, Faraday, had given to this body had been retained, as its relation to benzoic acid and benzoyl compounds is not any closer than it is to that of the tar or coal from which it is obtained."

Almost at the same time Pélégot found that the same hydrocarbon occurs, together with benzene,  $C_{13}H_{10}O$  (diphenylketone,  $CO(C_6H_5)_2$ ), in the products of the dry distillation of calcium benzoate.

The different results obtained by Mitscherlich and Pélégot are represented by the following formulæ :—



Pélégot obtained benzene only as a by-product, exactly as in the preparation of acetone (dimethylketone) from calcium acetate ; a certain quantity of marsh gas is always formed.

It is not clear how Liebig became acquainted with the fact that benzene is formed by the dry distillation of coal, as his pupil Hofmann, who obtained it in 1845 from coal-tar, observes : "It is frequently stated in memoirs and text-books that coal-tar oil contains benzene. I am, however, unacquainted with any research in which this question has been investigated." It is, however, worthy of remark that about the year 1834, at the time when Mitscherlich had converted benzene into nitrobenzene, the distillation of coal-tar was carried out on a large scale in the neighbourhood of Manchester ; the naphtha which was obtained was employed for the purpose of dissolving the residual pitch, and thus obtaining black varnish. Attempts were made to supplant the naphtha obtained from wood-tar, which at that time was much used in the hat factories at Gorton, near Manchester, for the preparation of "lacquer," by coal-tar naphtha. The substitute, however, did not answer, as the impure naphtha left, on evaporation, so unpleasant a smell that the workmen refused to employ it. It was also known about the year 1838 that wood-naphtha contained oxygen, whilst that from coal-tar did not, and hence Mr John Dale attempted to convert the latter into the former, or into some similar substance. By the action of sulphuric acid and potassium nitrate, he obtained a liquid possessing a smell resembling that of bitter almond oil, the properties of which he did not further investigate. This was, however, done in 1842 by Mr John Leigh, who exhibited

considerable quantities of benzene, nitrobenzene, and dinitrobenzene, to the Chemical Section of the British Association meeting that year in Manchester. His communication is, however, so printed in the Report that it is not possible from the description to identify the bodies in question.

Large quantities of benzene were prepared in 1848, under Hofmann's direction, by Mansfield, who proved that the naphtha in coal-tar contains homologues of benzene, which may be separated from it by fractional distillation. On the 17th of February 1856, Mansfield was occupied with the distillation of this hydrocarbon, which he foresaw would find further applications, for the Paris Exhibition, in a still. The liquid in the retort boiled over and took fire, burning Mansfield so severely that he died in a few days.

The next step in the production of colours from benzene and toluene is the manufacture of nitrobenzene,  $C_6H_5NO_2$ , and nitro-toluene,  $C_7H_7NO_2$ . The former compound, discovered in 1834 by Mitscherlich, was first introduced as a technical product by Collas under the name of artificial oil of bitter almonds, and Mansfield in 1847 patented a process for its manufacture. It is now used for perfuming soap, but mainly for the manufacture of aniline ( $C_6H_5NH_2$ ) for aniline blue and aniline black and for magenta. It is made on a very large scale by allowing a mixture of well-cooled fuming nitric acid and strong sulphuric acid to run into benzene contained in cast-iron vessels provided with stirrers.

To prepare aniline from nitrobenzene, this compound is acted upon with a mixture of iron turnings and hydrochloric acid in a cast-iron vessel. Commercial aniline is a mixture of this compound with toluidine obtained from toluene contained in commercial benzene. Some idea of the magnitude of this industry may be gained from the fact that in one aniline works near Manchester no less than 500 tons of this material are manufactured annually. From the year 1857, after Perkin's celebrated discovery<sup>1</sup> of the aniline colours, up to the present day, the history of the chemistry of the tar products has been that

<sup>1</sup> See Lectures by Professor Hofmann, F.R.S., "On Mauve and Magenta," 11th April 1862, and W. H. Perkin, F.R.S., "On the Newest Colouring Matters," 14th May 1869, *Proc. Roy. Inst.*; also President's Address (Dr Perkin, F.R.S.), *Journal of Society of Chemical Industry*, July 1885, "On Coal-Tar Colours" (p. 75, *ante*).

of a continued series of victories, each one more remarkable than the last.

### COAL-TAR COLOURS

To even enumerate the different chemical compounds which have been prepared during the last thirty years from coal-tar would be a serious task, whilst to explain their constitution and to exhibit the endless variety of their coloured derivatives which are now manufactured would occupy far more time than is placed at my disposal. Of the industrial importance of these discoveries, the speaker reminded his audience of the wonderful potency of chemical research, as shown by the fact that the greasy material which in 1869 was burnt in the furnaces or sold as a cheap waggon grease at the rate of a few shillings a ton, received two years afterwards, when pressed into cakes, a price of no less than one shilling per pound, and this revolution was caused by Graebe and Liebermann's synthesis of alizarin, the colouring matter of madder,<sup>1</sup> which is now manufactured from anthracene at a rate of more than two millions sterling per annum; and it is stated that an offer was once made, in the earlier stages of its history, by a manufacturer of anthracene to the Paris authorities to take up the asphalt used in the streets for the purpose of distilling it, in order to recover the crude anthracene.

Again, we have in the azo scarlets derived from naphthalene a second remarkable instance of the replacement of a natural colouring matter, that of the cochineal insect, by artificial tar-products, and the naphthol yellows are gradually driving out the dyes obtained from wood extracts and berries. It is, however, true that some of the natural dyestuffs appear to withstand the action of light better than their artificial substitutes, and our soldiers' red coats are still dyed with cochineal.

The introduction of these artificial scarlets has, it is interesting to note, greatly diminished the cultivation of cochineal in the Canaries, where, in its place, tobacco and sugar are now being largely grown.

Let us next turn to inquire as to the quantities of these various products obtainable by the distillation of one ton of coal

<sup>1</sup> "On the Artificial Production of Alizarin, the Colouring Matter of Madder," by Professor H. E. Roscoe, *Proc. Roy. Inst.*, 1st April 1870 (see p. 46, *ante*); also Dr Perkin, F.R.S., "On the History of Alizarin," *Journal Society of Arts*, 30th May 1879 (see p. 54, *ante*).



in a gas-retort. The six most important materials found in gas-tar from which colours can be prepared, are :—

- |             |                                       |
|-------------|---------------------------------------|
| 1. Benzene. | 4. Metaxylene (from solvent naphtha). |
| 2. Toluene. | 5. Naphthalene.                       |
| 3. Phenol.  | 6. Anthracene.                        |

The average quantity of each of these six raw materials obtainable by the destructive distillation of one ton of Lancashire coal is seen in Table I. Moreover, this table shows the average amount of certain colours which each of these raw materials yields, viz. :—

- |                         |  |
|-------------------------|--|
| 1. } Magenta, 0·623 lb. | 4. ( <i>Xylidine</i> , 0·07 lb.).      |
| 2. }                    | 5. Vermilline scarlet, 7·11 lbs.       |
| 3. Aurin, 1·2 lb.       | 6. Alizarin, 2·25 lbs. (20 per cent.). |

Further it shows the dyeing power of the above quantities of each of these colours, all obtained from one ton of coal, viz. :—

- |      |  |
|------|--|
| 1. } | Magenta, 500 yards of flannel 27 in. wide. |
| 2. } |  |
| 3.   | Aurin, 120 yards of flannel.               |
| 4. } | Vermilline scarlet, 2560 yards of flannel. |
| 5. } |  |
| 6.   | Alizarin, 255 yards Turkey-red cloth.      |

Lastly, to point out still more clearly these relationships, the dyeing power of one pound of coal is seen in the lowest horizontal column, and a parti-coloured flag, which exhibits the exact amount of colour obtainable from one pound of Lancashire coal, was exhibited.

Let us moreover remember, in this context, that no less than ten million tons of coal are used for gas-making every year in this country, and then let us form a notion of the vast colouring power which this quantity of coal represents.

The several colours here chosen as examples are only a few amongst a very numerous list of varied colour derivatives of each group. Thus we are at present acquainted with about sixteen distinct yellow colours ; about twelve orange ; more than thirty red colours ; about fifteen blues, seven greens, and nine violets ; also a number of browns and blacks, not to speak of mixtures of these several chemical compounds, giving rise to an almost infinite number of shades and tones of colour. These colours are capable of a rough arrangement according as they are originally derived from one or other of the hydrocarbons contained in the coal-tar. The fifty specimens of different colours exhibited

TABLE I.—ONE TON OF LANCASHIRE COAL YIELDS WHEN DISTILLED IN GAS RETORTS ON AN AVERAGE

Gas (cubic feet).	Ammoniacal liquor, 5° Tw.	Equal to ammonium sulphate.	Coal (gas) tar, sp. gr. 1·16.	Coke.					
10,000.	20 to 25 gallons.	30 lbs.	12 gallons = 139·2 lbs.	13 hundredweights.					
TWELVE GALLONS OF GAS TAR YIELD (Average of Manchester and Salford Tar).									
Benzene.	Toluene.	Phenol.	Solvent naphtha for indiarubber, containing the three xylenes.	Heavy naphtha.	Naphthalene.	Creosote.	Heavy oil.	Anthracene.	Pitch.
lb. 1·10 = aniline 1·10 = Magenta 0·623 or 1·10 lb. aniline yield 1·23 lb. methyl violet.	lb. 0·90 = toluidine 0·77	lb. 1·5 Aurin 1·2	lb. 2·44 yielding 0·12 xylene = 0·77 xylydine	lb. 2·40	lb. 6·30 = $\alpha$ -naphthylamine 5·25 = $\alpha$ - or $\beta$ -naphthol 4·75 = Vermilline scarlet, RRR 7·11 or = Naphthol yellow <sup>1</sup> 9·50	lb. 17·0	lb. 14	lb. 0·46	lb. 69·6
DYEING POWER OF COLOURS FROM 1 TON OF LANCASHIRE COAL.									
lb. 0·623 magenta dye 500 yards 27 in. wide flannel a full shade.	lb. 1·23 methyl dye 1000 yards 27 in. wide flannel a full violet.	lb. 9·50 naphthol yellow or dye 3800 yards 27 in. wide flannel a full yellow.	lb. 7·11 vermiline dye 2560 yards 27 in. wide flannel a full scarlet.	lb. 1·2 aurin dye 120 yards 27 in. wide flannel a full orange	lb. 2·25 alizarin 20% dye 255 yards printer's cloth a full Turkey-red.				
DYEING POWER OF COLOURS FROM 1 LB. OF LANCASHIRE COAL.									
Magenta or a piece of flannel 8 in. by 27 in.	Violet a piece of flannel 24 in. by 27 in.	Yellow or a piece of flannel 61 in. by 27 in.	Scarlet a piece of flannel 41 in. by 27 in.	Orange a piece of flannel 1·93 in. by 27 in.	Turkey-red a piece of flannel 4 in. by 27 in.				

<sup>1</sup> The naphthol yellow is a representative colour from  $\alpha$ -naphthol, while the vermiline scarlet is a representative colour from the combination of  $\alpha$ -naphthylamine with  $\beta$ -naphthol.

may thus be classified, but in this table, for the sake of brevity, only the commercial names and not the chemical formulæ of these compounds are given (see Table II.).

### AZO COLOURS

Amongst the most important of the artificial colouring matters may be classed the so-called azo colours. These colours are chiefly bright scarlets, oranges, reds, and yellows, with a few blues and violets. They owe their existence to the discovery by Griess, in 1860, of the fact that the so-called azo group  $-N=N-$  can replace hydrogen in phenols and amido compounds. But it is to Dr O. N. Witt that is due the honour of having given the first start in a practical direction to this class of azo colours by the discovery of chrysoidine, and perhaps still more so by the suggestions contained in a paper read before the Chemical Society. Dr Caro, of Mannheim, was also acquainted with several compounds which belong to this class at the time Witt published his results, but it does not appear that he made practical use of them until Witt introduced the chrysoidines and tropeolines. To Roussin, of the firm of Poirrier of Paris, is due the credit of having first brought into the market some of the beautiful azo derivatives of naphthol. Griess, therefore, as the original discoverer of the typical compounds and reactions by which the azo colours are obtained, may be considered as the grandfather, whilst Roussin and Witt are really the fathers, of the azo-colour industry. Nor must it be forgotten that it is to Perkin we owe the recognition of the value of the sulpho group in relation to azo colours, a discovery patented in 1863. Moreover it is interesting to note that changes in colour from yellow to red and claret are effected by the increase in the molecular weights of the radicals introduced as well as by the relative positions occupied by these groups.

### INDOPHENOL

Witt is also the discoverer of a new blue dyestuff termed indophenol, which has been used as a substitute for indigo. Certain difficulties, however, have arisen in the adoption of this colour on the large scale. The most important use indophenol is at present put to is for producing dark blues on reds dyed with azo colours, both on wool and cotton. The piece goods are

TABLE II.

Benzene.	Toluene.	Phenols.	Xylene.	Naphthalene.	Anthracene.
Orange yellow, or acid yellow	...	Picric acid	...	Manchester yellow (Dinitronaphthol)	Alizarin (pure)
Metanil yellow	...	...	...	Naphthol yellow	Anthrapurpurin
Auramine	...	...	...	...	...
Brown, Y	Bismarck brown, R	...	...	...	Flavopurpurin
Diphenylamine orange (Blackley orange)	...	...	...	...	...
Chrysoidine, Y	Chrysoidine, R	Aurin	...	...	...
Orange I.	...	...	...	...	...
Orange II.	...	...	...	...	...
Orange III. (helianthine)	...	...	...	...	...
Orange IV.	...	...	...	...	...
Safranine	Magenta, R	Eosin	...	Bordeaux	...
...	Magenta, B	Safrasin	...	Vermilline scarlet, R	...
...	...	Cyanosin	...	Vermilline scarlet, RRR	...
...	...	Rose Bengal	...	Vermilline scarlet, BBB	...
...	...	Phloxin	...	Roccellin	...
...	...	Erythrosin	(Mixture of xylene and naphthalene)	New red	...
...	...	...	Xylidine scarlet	Biebrich scarlet	...
...	...	...	(Mixture of cumene and naphthalene)	Crocein scarlet	...
...	...	...	Cumidine scarlet	...	...
Diphenylamine blue	Blackley blue, R	...	...	Victoria blue, 1	...
Methylene blue	Blackley blue, 1	...	...	Victoria blue, 5	...
Induline (Campbelline)	Alkali blue, R	...	...	...	...
...	Alkali blue, 6 B	...	...	...	...
Methyl violet, 6 B	...	...	...	...	...
Methyl violet, R	...	...	...	...	...
Malachite green	...	...	...	...	...
Brilliant green	...	...	...	...	...
Acid green	...	...	...	...	...

died a uniform red first, and then printed with indophenol white ; for like indigo itself indophenol yields a colourless body on reduction, and this being a very powerful reducing agent destroys the azo colour, being itself transformed into indophenol blue. The process works with surprising nicety and is very cheap. The blue is formed and the red discharged with such precision that patterns can be produced in which the blue discharge covers a great deal more space than the original red. This new printing process was devised by Mr H. Koechlin, of Lorrach. The reds used for the purpose are in the case of wool the usual azo scarlets, for cotton Congo red.

### ARTIFICIAL INDIGO

About five years ago the speaker had the honour of bringing before this audience<sup>1</sup> the remarkable discovery made by Baeyer of the artificial production from coal-tar products of indigo blue. Since that time but little progress has been made in this manufacture, as the cost of the process, unlike the case of alizarin, has as yet proved too serious to enable the artificial to compete successfully in the market with the natural indigo.

Through the kindness of a number of eminent colour manufacturers in this country and on the Continent, the speaker was enabled to illustrate his subject by a most complete series of specimens both of the colours themselves and of their application to the dyeing and printing of fabrics of all kinds. His thanks are especially due to his friend Mr Ivan Levinstein, of Manchester, for the interesting series of samples of cloth dyed with known quantities of fifty different coal-tar colours, each having a different chemical composition ; also to the same gentleman, and to Messrs Burt, Boulton, & Haywood, of London, for the interesting and unique series of specimens indicating the absolute quantities of products obtainable from *one ton of coal*, as well as for much assistance on the part of Mr Levinstein in the preparation of the experimental illustrations for this discourse. To Dr Martius of Berlin for a valuable series of colours, especially the well-known Congo red, made by his firm, including samples of wool dyed therewith, he is also much indebted. For the interest-

<sup>1</sup> "On Indigo and its Artificial Production," *Proc. Roy. Inst.*, 27th May 1881 (see p. 71, *ante*).

ing details concerning indophenol and its applications the speaker owes his thanks to Dr Witt and M. Koechlin.

### COAL-TAR ANTIPYRETIC MEDICINES

Next in importance to the colour industry comes the still more novel discovery of the synthetical production of antipyretic medicines.

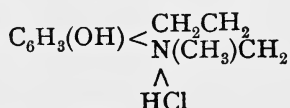
Up to this time quinine has held undisputed sway as a febrifuge and antiperiodic, but the artificial production of this substance has as yet eluded the grasp of the chemist. Three coal-tar products have, however, been recently prepared which have been found to possess strong febrifuge qualities, which if still in some respects inferior to the natural alkaloids, yet possess most valuable qualities, and are now manufactured in Germany at Höchst and at Ludwigshafen in large quantity. And here it is well to call to mind that the first tar colouring-matter discovered by Perkin (mauve) was obtained in 1856 during the prosecution of a research which had for its object the artificial production of quinine.

In considering the historical development of this portion of his subject, the speaker added that it is interesting to remember that the initiative in the production of artificial febrifuges was given by Prof. Dewar's discovery in 1881 that quinoline, the basis of these antipyretic medicines, is an aromatic compound, as from it he obtained aniline. Moreover, Dewar and McKendrick were the first to observe that certain pyridine salts act as febrifuges. So that these gentlemen may be said to be the fathers of the antipyretic medicines, as Witt and Roussin are of the azo-colour industry.

*Kairine*, the first of these, was discovered by Prof. O. Fischer, of Munich, in the year 1881, whilst engaged on his investigations of the oxyquinolines. The febrifuge properties of this substance were first noticed by Prof. Filehne of Erlangen. *Kairine* is manufactured from quinoline, a basic product derived from aniline by heating it with glycerin and nitrobenzene by the following process. When treated with sulphuric acid, it forms quinoline sulphonic acid, and this when fused with caustic soda yields oxyquinoline, which is then reduced by tin and hydrochloric acid into tetrahydroxyquinoline, and this again on treatment with ethyl bromide yields ethyl tetraoxyquinoline or *kairine*.

The lowering of the temperature of the body by this compound is most remarkable, though, unfortunately, the action is of much shorter duration than that effected by quinine itself; but on the other hand, with the exception of its burning taste, it exerts no evil effects such as are often observed after administration of large doses of quinine. The commercial article is the hydrochloride, the price is 85s. per lb., and the quantity manufactured has lately diminished owing to the discovery of the second artificial febrifuge, antipyrine.

The following graphical formula shows the constitution of kairine :—



*Antipyrine*, the second of these febrifuges, was discovered in 1883 by Dr L. Knorr in Erlangen, and its physiological properties were investigated by Prof. Filehne of Erlangen. The materials used in the manufacture of antipyrine are aniline and aceto-acetic ether. The aniline is first converted into phenylhydrazine, a body discovered by Emil Fischer in 1876. This body combines directly with aceto-acetic ether, with separation of water and alcohol, to form a body called pyrazol ( $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ ). The methyl derivative of pyrazol derived by treating it with iodide of methyl, is antipyrine, its composition being  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ . As a febrifuge, antipyrine is superior in many respects to kairine and even to quinine itself. It equals kairine in the certainty of its action, whilst in its duration it resembles quinine. It is almost tasteless and odourless, is easily soluble in cold water, and takes the form of a white crystalline powder. Its use as a medicine is accompanied by no drawbacks. It occurs in commerce in the free state. The production of antipyrine, in spite of these valuable qualities, is as yet small, its chief employment being in Germany, where it has been successfully used in cases of typhoid epidemic. The price is 6s. per lb.

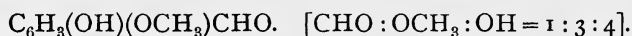
*Thalline*, the third of the artificial febrifuges, is offered as the tartrate and sulphate. It is manufactured by the Badische Company. Thalline is said to be used as an antidote for yellow fever. Its scientific name is tetrahydroparaquinanisol, and it was first prepared by Skraup by the action of methyl iodide and potash on paroxyquinoline.

We must, however, bear in mind that none of these synthetical febrifuges are antiperiodics, and therefore cannot be employed instead of the natural alkaloid quinine in cases of ague or intermittent fevers.

### COAL-TAR AROMATIC PERFUMES

A third group of no less interest comprises the artificial aromatic essences, and of these may here be mentioned, in the first place, *cumarin*,  $C_9H_6O_2$ , the crystalline solid found in the sweet woodruff, in Tonka bean, and in certain sweet-scented grasses. This is now artificially prepared by acting upon sodium salicyl aldehyde with acetic anhydride by the reaction which is associated with the name of Dr Perkin, and is used in the manufacture of the perfume known as "extract of new-mown hay."

A second interesting case of a production of a naturally occurring flavour, is the artificial production of *vanillin*, the crystalline principle of vanilla. Vanilla is the stalk of the *Vanilla planifolia*, which encloses in its tissues prisms of crystalline vanillin, to which substance it owes its fragrance. Tiemann and Harrmann showed that vanillin is the aldehyde of methyl protocatechuic acid.



The chief seats of the vanilla productions are on the slopes of the Cordilleras north-west of Vera Cruz in Mexico, also the island of Réunion, and in the Mauritius. Since the discovery of the artificial production of vanillin, the growth of the vanilla has been very much restricted.

A variety of vanilla, termed vanillon, obtained in the East Indies, has long been used in perfumery for preparing "essence of heliotrope." This contains vanillin together with an oil, which is probably oil of bitter almonds. The essence of white heliotrope is now entirely prepared by synthetical operations. It is manufactured by adding a small quantity of artificial oil of bitter almonds to a solution of artificial vanillin; when these substances are allowed to remain for some time in contact, the mixture assumes an odour closely resembling that of natural heliotrope.



VIII.: 1886

## THE SCIENTIFIC DEVELOPMENT OF THE COAL-TAR COLOUR INDUSTRY

BY PROFESSOR R. MELDOLA, F.C.S., F.I.C.

(*Journal of the Society of Arts*, 1886, p. 759)

IT will, I think, be conceded that the manufacture of coal-tar products is *par excellence* the most scientific of the chemical industries. This high position may fairly be claimed for the industry when we consider the number and complexity of the products, the delicacy of many of the reactions employed, the special arrangement of plant required, and the intimate knowledge of the chemistry of the aromatic compounds which the colour chemist must at the present time possess. Moreover, the industry is of comparatively recent growth—it has been born and has reached its present development within the last thirty years, so that the successive phases of its evolution can be clearly traced. For these reasons the subject is well calculated to throw light upon the general question of technical chemical education, a question of which the importance to the country at large now bids fair to become duly recognised.

In the brief historical sketch which I now propose to lay before you, I shall mention only those discoveries which may be considered to mark distinct commercial epochs in the development of the industry. The successive steps in this development will furnish us with one of the most striking illustrations of the utilisation of scientific discovery for industrial purposes, and the reaction of industry upon pure science.

Commencing in the year 1856, the foundation of the coal-tar colour industry was laid by Perkin, by the discovery of mauve,

a violet dye, obtained accidentally in the course of an investigation having for its object the preparation of quinine by an artificial synthesis. In 1860, magenta, which had formerly been made in small quantities by expensive processes, was rendered a product of the first order of commercial importance, by the discovery of the arsenic acid process by Medlock and E. C. Nicholson simultaneously. During this same year, phenylated blues were first produced by Girard and De Laire, by the action of aniline upon a magenta base at a high temperature. These blues had but a limited application owing to their insolubility, and their value was enormously enhanced by Nicholson's discovery in 1862, that these colours could be converted into soluble sulphonic acids. The first azo colour, amido-azobenzene, a basic yellow dye, was introduced in 1863, by the firm of Simpson, Maule & Nicholson, under the name of aniline yellow. In this same year the methylic and ethylic derivatives of magenta were manufactured by the same firm, under the name of Hofmann violets, in honour of their discoverer. Azodiphenyl blue, the first of the colouring matters now known as indulines, and Manchester yellow, appeared in 1864; and in 1866 Bismarck brown (triamidoazobenzene) was first manufactured at Manchester. The same year (1866) was marked by the introduction of Coupier's nitrobenzene process for the manufacture of magenta. In 1868, Graebe and Liebermann gave to the world their great discovery of the chemical constitution of alizarin, and in the following year the manufacture of this colouring matter from anthracene was commenced. The first members of the great family of the "phthaleines," viz. gallein and fluorescein, were discovered by Baeyer in 1871; and the first technical application of this discovery was made in 1874 by Caro, who introduced the beautiful pink tetrabromfluorescein into commerce, under the name of eosin. Diamidoazobenzene was discovered by Caro and Witt independently in 1875, and was introduced into commerce by the latter as chrysoïdine. A great impetus was given to the technical production of azo-colouring matters by this discovery, the naphthol oranges and other "tropæolines," fast-red, the ponceau scarlets, etc., appearing in 1878. Methylene blue and acid magenta were introduced by Caro in 1877, and in the same year the old and fugitive aniline yellow was converted into a valuable acid yellow by Grässler, who patented a process for converting the base into a sulphonic acid. Malachite green

was introduced in 1878, and in 1879 the first member of the now important group of secondary azo compounds appeared under the name of Biebrich scarlet. It is these secondary azo scarlets, and especially the croceine scarlets (discovered in 1881), which are exterminating the cochineal industry. The year 1880 was marked by the brilliant discovery of the constitution of indigo, and the synthesis of this colouring matter by Baeyer, a discovery which is none the less a triumph of synthetical chemistry because the manufacture is not at present successful from a commercial point of view. Indophenols were introduced by Koechlin and Witt in 1881, and in 1883 appeared Caro's first patent for the production of colouring matters of the rosaniline group by the method of "condensation" with phosgene gas, in the presence of suitable condensing agents.

This chronological record comprises nearly all the chief colouring matters from coal-tar which are or have been of industrial value. It is important to note that the list, even as it stands in the form of a bald statement of facts in chemical history, reveals the existence of that fundamental law of the "survival of the fittest." Old products have been displaced by newer ones, as fresh discoveries were made, or processes improved, and to the chemist it is of interest to observe how this development of an industry has gone on *pari passu* with the development of the science itself. The moral conveyed to the manufacturer is sufficiently obvious. If we are to recover our former supremacy in this industry, we must begin by dispelling conservative ideas—we must realise the fact that no existing process is final, and that no product at present sent into the market is destined to survive for an unlimited period. The scientific manufacturer must be brought to see that present success is no guarantee for future stability, and unless he realises this position in its fullest significance, he may find the sale of his standard products gradually falling off, or be compelled to wake up to the unpleasant fact that his competitors are underselling him, owing to improved methods of manufacture.

It may appear to many that I am here simply preaching the doctrine of progress, and that the remarks which I have offered are mere truisms. Unfortunately, the facts of the case render this appeal necessary. It must never be forgotten that the coal-tar colour industry is essentially of English origin. It was Faraday who first discovered benzene in 1825; it was Mansfield

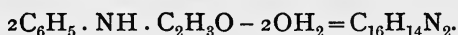
who, in 1847, first isolated this substance in large quantities from coal-tar, and showed how nitro-benzene could be manufactured therefrom. The beginning of the colour industry was Perkin's discovery of mauve; and the introduction of the new colour into dyeing establishments was due to the example set by Messrs Pullar, of Perth, in 1856. The manufacture of magenta on a large scale was the result of the discovery of the arsenic acid process by Medlock and Nicholson; and the phenylic blues were made commercially valuable by Nicholson. The first azo colours, aniline yellow and Manchester brown, as well as Manchester yellow (dinitro-*a*-naphthol), were manufactured in this country. We may thus fairly lay claim to have given to the commercial world the types of all the more important colouring matters of the present time. If, as is certainly the case, the development of these typical products has been allowed to take place in other countries, it behoves us, as a practical nation, to inquire closely into the cause of this success abroad, a success which will appear all the more remarkable when we bear in mind that we are the largest European producers of the raw material, gas tar, out of which the colours are manufactured, as well as being among the largest consumers of the dyes themselves. It is estimated that the amount of tar distilled annually in this country is about 500,000 tons, and it is certain that we distil at least one-half of the whole amount of tar produced in Europe. The present state of affairs is that our competitors can afford to import the raw materials from us, to manufacture and return the colours so as to compete with us successfully in our own markets, and to undersell us in the foreign markets. The bare mention of these facts will be sufficient to indicate the existence of something requiring radical reform in our manufacturing system.

Before submitting to you the statistics of this industry which I have been able to collect, I think it is desirable to make an attempt to show the inner mechanism by which chemical science has been and is being so successfully adjusted to commercial wants by our Continental neighbours. I regret exceedingly that my predecessors on this and other platforms have not left me the chance of giving a general sketch of the chemical development of the different groups of colouring matters. In fact, I find myself suffering here from several distinct disadvantages, but I hope, with your forbearance, to make the best of the situation.

It will serve my purpose equally well, or perhaps even better, to confine my illustration to one particular group of colouring matters. The more striking achievements, such as the syntheses of alizarin and indigo, are now so familiar to chemical audiences, that their repetition would be unnecessary. Equally instructive, from the present point of view, would be the history of the colouring matters of the rosaniline group, and I can only express a passing regret that time will not permit me to recapitulate the steps in the beautiful series of investigations which led to the establishment of the structural formula of rosaniline and its derivatives by E. and O. Fischer, and then to the synthesis of these colours by Caro from ketone bases. The principle which I wish to bring out may seem a strange one to a "practical" people, but I am convinced that the whole secret of success abroad is the spirit of complete indifference to immediately successful results in which the researches are carried on. I say, "immediately successful," because it would of course be absurd on the part of an investigator not to take advantage of any discovery which happened to be of commercial value. But, as a general principle, the question of practical utility does not in the first place enter into the work. The great development of this and many other industries is mainly due to the complete and thorough recognition, on the part of our competitors, of the vital importance of chemical science. In this country, where the word "practical" threatens to become a reproach, we put science into the background, and attach all importance to the mere technique of our manufactures. If I might venture to offer an aphorism to the English manufacturer, it would be to the effect that he should look after the science, and leave the technique to take care of itself.

After these considerations, you will see that it is a matter of perfect indifference whether I take by way of illustration products which have been successful from a financial point of view or not. In order to give greater emphasis to the principle, I propose, however, to consider the history of some colouring matters which have found a market value, and I select this group with the more readiness because, on the one hand, it was not treated of last year by Dr Perkin, and, on the other hand, it furnishes a splendid illustration of the way in which these coal-tar products are being scientifically developed in the foreign laboratories.

In 1863, Mr E. C. Nicholson discovered a basic orange colouring matter among the by-products formed during the manufacture of magenta by the arsenic acid process. The method of isolating this substance in a state of purity was very skilfully worked out by Messrs Simpson, Maule & Nicholson, and the colour was introduced into the market under the name of phosphine. This dye was the first basic orange discovered, and the advantages which it possessed for certain kinds of dyeing enabled the manufacturers to sell it at a price which helped to cheapen the cost price of magenta to an appreciable extent. The chemical composition of the substance was established in 1863 by Hofmann, who assigned the formula  $C_{20}H_{17}N_3 \cdot H_2O$ , and described the base under the name of chrysaniline. Although other and cheaper basic orange colouring matters have since been discovered, chrysaniline still finds a distinct use; and I am informed by Messrs Brooke, Simpson & Spiller that the amount of this colour now sold is not appreciably less than at the time of its introduction by their predecessors. The chemical constitution of chrysaniline remained unknown till about two years ago, when the problem was solved by O. Fischer (*Ber.*, 1884, p. 203). In order to be able to follow the steps in the investigation, it will be necessary, in the first place, to go back to the discovery of another colouring matter, called flavaniline, of which the existence was made known by O. Fischer and C. Rudolph in 1882 (*Ber.*, 1882, p. 1500). Flavaniline was produced by the action of dehydrating agents, such as zinc chloride, upon acetanilide, this fact having been observed by Rudolph in 1881, and the practical manufacture of the colour having been carried on under a patent by Messrs Meister, Lucius & Brünig, of the Hoechst colour works.<sup>1</sup> Supplied with a large quantity of the pure crystalline material by the manufacturers, Messrs Fischer and Rudolph established the formula of flavaniline,  $C_{16}H_{14}N_2$ , and showed that its formation from acetanilide might be expressed by the equation :

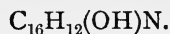
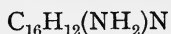


By the action of nitrous acid upon flavaniline a diazo compound was produced which, by the usual method of decomposition by water, gave a phenolic derivative termed flavenol, possessing

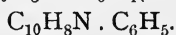
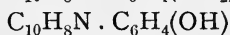
<sup>1</sup> I am indebted to this firm for having kindly supplied me with specimens of these products for exhibition.

the formula  $C_{16}H_{12}N.OH$ , thus proving that flavaniline contained a displaceable  $NH$  group. By heating flavenol with zinc dust, a base was obtained having the formula  $C_{16}H_{13}N$ , and termed flavoline. This base had an odour resembling that of quinoline, and all its properties suggested to the authors that flavaniline was in reality a quinoline derivative. That flavaniline was amido-flavoline was proved by nitrating the latter base, and reducing the nitro compound, when flavaniline was obtained. In a later publication by Besthorn and Fischer (*Ber.*, 1883, p. 68) it was announced that flavenol, when oxidised by potassium permanganate in an alkaline solution, gave an acid which, on distilling with lime, furnished a base having all the characters of lepidine. By the continued oxidation of flavenol with excess of alkaline permanganate, another acid was obtained, which proved to be picoline-tricarboxylic acid, and the latter, on further oxidation, gave picoline-tetracarboxylic acid (*Ber.*, 1884, p. 2925).

So much for the facts ; now for their interpretation. The production of flavenol from flavaniline by the diazo reaction shows that the respective formulas of these substances are :



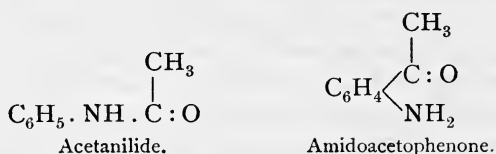
Flavenol gave, as the first product of oxidation, lepidine-carboxylic acid, of which the formula is  $C_{10}H_8N(CO_2H)$ , and by further oxidation it gave picoline-tricarboxylic acid, of which the formula is  $C_6H_4N(CO_2H)_3$ . Now the C-atoms oxidised by the breaking down of the 16-carbon atom flavenol into 11-carbon atom lepidine-carboxylic acid, are those C-atoms which in flavenol are associated with the hydroxyl group, because this group is no longer contained in the product of oxidation. Thus the formulas of flavaniline, flavenol, and flavoline are better expressed as :



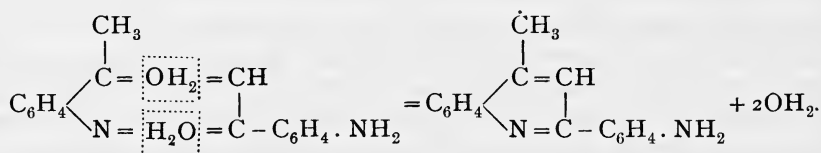
From this it appears that flavaniline is amidophenyl-lepidine, flavenol hydroxyphenyl-lepidine, and that flavoline is phenyl-lepidine.

The central nucleus of flavaniline having thus been shown to be lepidine (which is methylquinoline), the next question to be settled was the mode of formation of the colour base from acetanilide. The authors suggest that at the high temperature

of the reaction, acetanilide, in the first place, becomes transformed into the isometric orthoamidoacetophenone :



By the condensation of two molecules of the amidoacetophenone with the elimination of two molecules of water, flavaniline would be produced in a manner analogous to the formation of mesitylene by the condensation of three molecules of acetone under the influence of dehydrating agents :



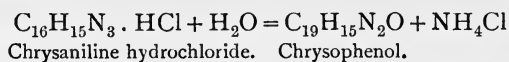
The accuracy of this suggestion was verified by showing that orthoamidoacetophenone is present in small quantity when the reaction is arrested as soon as the formation of colouring matter commences ; and conversely, when pure orthoamidoacetophenone was heated with zinc chloride, flavaniline was produced in small quantity.

We may be permitted to pause at this stage of the investigation before proceeding to consider the connection of this work with the constitution of chrysaniline. These results cannot but be regarded by chemists as a very beautiful piece of investigation ; but the person of a "practical" turn of mind may possibly want to know what bearing they have upon the question of market value—the question which the manufacturer but too frequently considers as the only one of importance. Now, it is the essence of chemical science—as indeed of all other sciences—that every discovered fact is related to other groups of facts, and, although the relationship may not at once be apparent, it is only a matter of further development that is necessary in order to reveal relationships which are obscure on account of our imperfect knowledge. Thus the policy of looking at a chemical product from the narrow point of view of immediate utility is not only unscientific, but it is detrimental to the interests of the manu-



facturer himself. Every new compound or process discovered—every structural formula established by legitimate investigation—may have an enormous influence, directly or indirectly, upon the market value of products at present sent into commerce. Our manufacturers must realise this if they wish to recover their position in the coal-tar industry, or in fact in any other chemical industry. There is no branch of manufacture so perfect as not to be open to further improvement, and until the broad spirit of scientific development is made to replace the suicidal policy of immediate utility, our position as a manufacturing nation is not likely to be improved.

In order to justify this digression by the particular instance now under consideration, we must return to the work of Messrs Fischer and Besthorn. The discovery that flavaniline was a quinoline derivative was of importance as a principle, quite apart from any immediate value attaching to the dyestuff itself. Up to the time of this discovery, the quinoline derivatives had been practically of no importance in the tinctorial industries, but as a consequence of the present investigation the question at once suggested itself whether the analogous bases of high boiling-point, which are present in coal-tar, such, for example, as acridine, might not be utilised as sources of colouring matters. I may remind you that the fact of quinoline being an aromatic compound was first established by the researches of our Chairman this evening, Professor Dewar, who obtained aniline from this base. In a subsequent paper on chrysaniline (O. Fischer and G. Körner, *Ber.*, 1884, p. 203), it was pointed out that in the course of his investigations upon rosaniline Fischer had observed that the former base, like rosaniline, was capable of furnishing a diazo compound. An observation made by Claus is also mentioned, viz. the conversion of chrysaniline into a phenol (chrysophenol) by heating to a high temperature with hydrochloric acid in accordance with the equation :

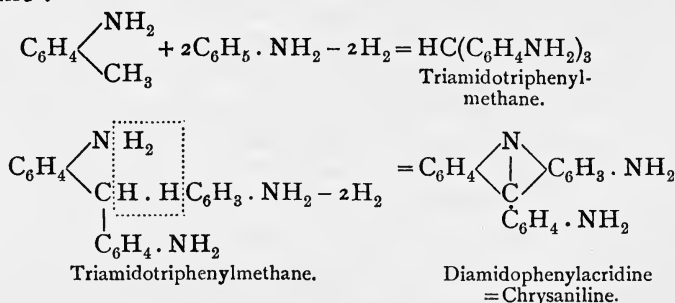


The investigation of flavaniline appears to have given an impetus to the ideas respecting chrysaniline, because of the general similarity in the properties of these two substances. In confirmation of this impression, it was found that by the oxidation of chrysophenol an acid was obtained which, on distillation

with lime, gave a pyridine base. I need hardly remind you that picoline, which was obtained from the acid resulting from the extreme oxidation of flavenol, is methylpyridine. It was thus established that chrysaniline was a derivative of a quinoline base.

The next step in the investigation is a very important one. By decomposing the diazo compound of chrysaniline with alcohol according to the Griess reaction, phenylacridine was obtained. Acridine is a base belonging to the quinoline series, having the formula  $C_{13}H_9N$ . It was discovered by Graebe and Caro in 1872 in crude anthracene. Phenylacridine accordingly possesses the formula  $C_{13}H_8N \cdot C_6H_5$ ; and chrysaniline appears as diamidophenylacridine— $C_{13}H_7(NH_2)N \cdot C_6H_4(NH_2)$ , because two amido groups are replaced by H by the diazo reaction. Thus the formula  $C_{20}H_{17}N_3$  (first assigned by Hofmann to chrysaniline) is really the formula of the higher homologue, chrysotoluidine.

In order to explain the formation of chrysaniline during the oxidation of the materials (aniline and toluidine) in the "red melt" still, several suggestions were put forward, of which the most probable appeared to be that the base was derived from triamidotriphenylmethane, the latter compound resulting from the condensation of two molecules of aniline with one of ortho-toluidine :



The relationship of chrysaniline to the colouring matters of the rosaniline group is thus indicated; but, tempting as is this theme, time will not admit of further digression into this field. The main point, so far as we are at present concerned, is that by means of the present investigation we have now arrived at a knowledge of the parent substance, acridine, of which a colouring matter more than twenty years old proves to be a

derivative. By such results new fields of investigation are opened up, and direct methods for the production of chrysaniline suggest themselves. Even the practical requirements would be satisfied if it could be shown that the colour could be manufactured cheaply by a direct synthesis, instead of depending, as heretofore, upon the small and capricious secondary product of the magenta manufacture. As a matter of fact, several syntheses of chrysaniline have been effected, one of which forms the subject of a patent (German patent, 29142, April 1884) by Messrs Ewer & Pick, of Berlin. Into the mode of preparation by this patented process I cannot now enter any further than by merely stating that nitrodiphenylamine and nitrobenzoylchloride form the starting-points, and that the specification bears the title, "preparation of chrysaniline and other colouring matters of the phenylacridine group." If an elaborate scientific investigation culminates in a patent, its utility will, I know, be conceded by many for whom the work would otherwise have possessed no particular interest.

The illustration which I have given is a typical example of the kind of scientific development which is being carried on by our chemical colleagues abroad, and which is being taken advantage of in the Continental factories. I do not wish to give you the impression that the particular colouring matters dealt with are of supreme importance industrially—they are of considerable importance, but the modern history of any other colouring matters would have been equally instructive. The beautiful researches of Bernthsen upon the constitution of methylene blue would have done equally well had time permitted of my making use of them.

It was stated at the commencement of this paper that there is reason to believe that our supremacy in the coal-tar colour industry has, for some years, been declining, and I have further expressed my belief that the chief cause of this falling off is the subordinate position given to chemical science in this country as compared with the status of this science abroad. Whether this explanation be accepted or not, the fact of the decadence of the manufacture remains, and I am in a position to bring this unpleasant truth home to our countrymen by a strong body of evidence. It must be borne in mind that the decline of any industry cannot be measured by the absolute weight of the products turned out annually, because the demand for the pro-

ducts in question may be on the increase, and we may be actually producing a greater weight of colours now than we were during our most successful period. The whole question is a relative one: it is simply, how much material are we now turning out as compared with the amount produced by our competitors—what proportion of coal-tar products do we supply for our own and foreign consumption? In order to answer this question with some approach to numerical exactness, it occurred to me that the most trustworthy information could be obtained from the consumers themselves; and through the kindness of Mr Robert Pullar, of Perth, and Mr Ernest Hickson, of Bradford, I have been enabled to put myself into communication with several of the representative dyeing and printing establishments of this country. The facts obtained, as showing the actual state of the industry at the present time, appear to me of sufficient interest to be given here in some detail. I may take the present opportunity of stating that my application for statistical information has been most courteously responded to by the various firms, to whom I have great pleasure in returning my thanks.

Edward Ripley & Son, of Bradford, perhaps the largest dyers of piece goods in the kingdom, inform me that during the year 1885 they used  $86\frac{1}{2}$  per cent. of foreign coal-tar colours, and  $13\frac{1}{2}$  per cent. of English make.

Walter Walker & Son, of Dewsbury, dyers of wool for rugs, mats, carpet yarn, and blanket stripes, estimate that during 1885 they used 80 per cent. of German dyes. They state that the exact proportion is difficult to estimate, so that the figure given is only approximative. Referring to their larger consumption of foreign colour, they state: "It is very discouraging to have to do this and send the trade out of our country, but to our own interest and advantage we have to do it."

John Newton, silk dyer, Macclesfield. Mr Walter Newton, F.C.S., informs me that during 1885 they used 80 per cent. of foreign colour. He adds: "The rapid advancement in the improved manufacture of some of these dyes by the Germans is the only cause of our desertion from the English colour manufacturer."

G. W. Oldham, silk dyer, of Netherton, near Huddersfield, informs me that during 1885 he used 2000 lbs. of German dyes, 1100 lbs. of English dyes, and 800 lbs. of doubtful origin.

James Templeton & Co., of Glasgow, state that they dye as much as 30,000 lbs. of yarn (chiefly worsted) weekly, but they use only a small proportion of coal-tar dyes, all of which are of German manufacture.

Messrs Leckie & MacGregor, of Paisley, inform me that in the west of Scotland, including Glasgow and Paisley, they are certain that at least 90 per cent. of the dyes used come from the Continent. Their own consumption of English colour only reached 6·8 per cent.

Alexander Harvey & Son, of Glasgow, yarn dyers, state that during 1885 they used 60 per cent. of German and 40 per cent. of English dyes. These figures do not include alizarin, of which they state that they used about equal quantities of German and English make. The English supply is chiefly made up of one article, "aniline salt." They add: "We find the German makes in general of better value than the British, as our rule is, *ceteris paribus*, to give the home-make the preference."

Messrs Manson & Henry, Glasgow, yarn dyers, state that they use only German dyes, adding that they find it to their advantage "for both cheapness and quality."

Among the largest consumers of coal-tar colours in this country are the jute dyers. As representing this department of the tinctorial industry, Messrs James Stevenson, of Dundee, inform me that during 1885 they used only 7·7 per cent. of English colour. They have been good enough to supply the following analysis of their consumption:—

Scarlet . . .	37	per cent., of which nothing is English.		
Crimson . . .	16	"	6·4	"
Blues . . .	11·5	"	nothing	"
Oranges . . .	11	"	0·5	"
Greens . . .	7	"	nothing	"
Magenta (residues)	6·5	"	"	"
Maroon . . .	5·5	"	"	"
Pink . . .	2·75	"	"	"
Brown . . .	1·25	"	1·25	"
Violet . . .	1	"	nothing	"
Various . . .	0·5	"	"	"
	<hr/>		<hr/>	
	100·0		7·7	

Messrs Cox Bros., of the Camperdown Jute Works, Lochee, state that practically the whole of the "aniline" colours used by them are of Continental manufacture.

With reference to the calico-printers, the following facts have been collected :—

Messrs Z. Heys & Sons, of Barrhead, state that during 1885 they used over 10,000 lbs. weight of colours (exclusive of alizarin), of which 700 lbs. only were of English make.

Messrs James Black & Co., of Bonhill, Dumbartonshire, state that in their belief more than one-half of the colour used by calico-printers is of foreign manufacture.

In the course of the present inquiry it seemed desirable to obtain information concerning the consumption of alizarin, with reference to which the following statements have been received :—

Messrs Walter Crum & Co., of Thornliebank, Glasgow, are of opinion that “the great bulk of what is used in this country is manufactured in Germany.” They do not profess to be able to give actual figures having any approach to accuracy.

Mr John Christie, of the Alexandria Turkey-Red Works, Dumbartonshire (John Orr-Ewing & Co.), states that they use only artificial alizarin in their establishment, their consumption being considerably over two million lbs. weight of 10 per cent. paste annually. Their consumption was in—

1880 .	.	98 per cent. German.	2 per cent. English.
1881 .	.	90     ”     ”	1     ”     ”
1882 .	.	100    ”     ”	0     ”     ”
1883 .	.	77     ”     ”	23    ”     ”
1884 .	.	56     ”     ”	44    ”     ”
1885 .	.	47     ”     ”	53    ”     ”

Messrs William Stirling & Sons, of Glasgow, state that their relative consumption of English and German alizarin for Turkey-red dyeing varies so much from year to year that they have no means of directly supplying useful data. This firm has, however, been good enough to make inquiries for me from a competent authority, who has furnished the following report :—

“In 1883 and 1884, I estimate that the sales (of alizarin) in the United Kingdom amounted to a monthly average of about 530 tons, 10 per cent. (say, 6360 tons, 10 per cent. per annum). Of this quantity, I estimate about 30–33 per cent. was manufactured in this country. Taking 1884 alone, the figures are estimated at 566 tons, 10 per cent. per month (say, 6800 tons, 10 per cent. per annum). Proportion manufactured in Great Britain, say, about 30–35 per cent. In 1886, the consumption may be estimated at 550–600 tons, 10 per cent. per month (say,

6900 tons, 10 per cent. per annum). Proportion manufactured in this country probably now very considerably more than 35 per cent."

This estimate of the total consumption (550–600 tons, 10 per cent. per month) is confirmed by my friend Mr Thomas Royle, F.C.S., of the British Alizarin Company's works at Silvertown, but he is of opinion that 50 per cent. of this is of English manufacture.

By way of further confirmation, it appeared to me to be desirable to get the opinion of manufacturers themselves, and although this has been a matter of considerable difficulty, I am able to give some kind of an estimate. Mr Ivan Levinstein, of Manchester, estimates that Germany produces :

Colours derived from benzene and toluene, six times more than England.

Colours derived from naphthalene, seven times more than England.

Colours derived from anthracene, five times more than England.

The average production of Germany is thus about six times that of this country. Mr W. A. Mitchell, of the firm of W. C. Barnes & Co., Phoenix Works, Hackney Wick, informs me that of some 159 tons of "aniline" dyes which passed through their hands as agents last year, 95 per cent. were of Continental make. With reference to the two chief raw materials, benzene and aniline, this same firm estimates that about 75 per cent. of the whole quantity of these products made in England goes to the Continent.<sup>1</sup>

The facts and figures which I have now laid before you must be left to tell their own story—time will not permit me to attempt any analysis of them. The evidence collected will at any rate give a much more forcible idea of the true state of the coal-tar colour industry in this country than has hitherto been attempted, and if this evidence goes against us as a manufacturing nation, it is all the more desirable that our true

<sup>1</sup> According to a later estimate, kindly supplied by Mr Ivan Levinstein the quantity of benzene and toluene used in this country amounts to about half a million gallons, and that used in Germany to about two million gallons annually. About half the English production is, however, exported as aniline, toluidine, and aniline salt, while Germany converts into colouring matters at least 1,600,000 gallons of these hydrocarbons.

position should be realised. I find that it is almost impossible to give a correct numerical expression in pounds sterling for the annual value of this industry to the country, as the estimates vary within very wide limits. According to Dr Perkin, whose opinion on this matter will perhaps carry the greatest weight, the value of the annual output is between £3,000,000 and £4,000,000. That the industry is one of considerable importance on the Continent may be gathered from the official returns relating to the German exports. For the following figures I am indebted to Dr H. Caro, of the Badische Anilin- und Soda-Fabrik, Ludwigshafen on Rhine :—

EXPORTED FROM GERMANY, FROM JANUARY 1 TO DECEMBER 31, 1885.

Alizarin paste (? per cent.) . . . . .	4283 tons.
Aniline and intermediate products. . . . .	1713 „
Aniline, etc., colours . . . . .	4645 „

Dr Caro adds that it is generally believed that about four-fifths of the entire German production are exported.

The magnitude of this branch of chemical industry abroad will be gathered from the fact that a German factory of about the third magnitude consumes at the present time between 500 and 600 tons of aniline annually. According to information recently furnished to me from the two largest of the German factories, the Badische Company employ 2500 working men and officials, and the Hoechst Colour Works (formerly Meister, Lucius & Brüning) 1600 working men and fifty-four chemists. It must of course be borne in mind that in these factories the products are not “aniline” colours only, but alizarin, acids, alkalies, and all chemicals required in this branch of manufacture.

The industry which has been selected for this evening's topic is thus not only an important one in itself, but for us, as chemists, its development is fraught with meaning both scientifically and educationally. In taking up this subject it has not been my desire to exalt the coal-tar colour industry to a position of undue importance, nor do I wish it to be inferred that the remarks which I have made concerning its decadence, or at any rate stagnation, in this country are applicable to this manufacture only. The failure on our part to grasp the true spirit of chemical science in its relation to our manufactures makes itself felt in every industry in which chemistry is concerned. The strength of our competitors is in their laboratories, and



not, as here, upon the exchanges. It is only by showing up our weakness in each industry that the state of affairs can be remedied, and our prestige as a manufacturing country restored. If each specialist would do for his industry what I have here attempted to do broadly for the coal-tar colour industry, we should get together a body of evidence which the Royal Commissioners on the depression of trade would do well to take into consideration. We have heard a great deal of late years about the subject of technical education, but the talk has been rather one-sided. We have had utterances from those who, recognising the enormous importance of this subject to the country, have munificently endowed those institutions for the promotion of technical education which are springing up around us ; we have had all kinds of schemes from those who are taking upon themselves the duties of technical educators ; but it appears to me that we have not heard with sufficient distinctness the voices of those who may be presumed to suffer most from the want of technical education, viz. the manufacturers themselves. I have heard rumours of the existence of a certain class of manufacturer—let us hope a rare species—who declares that science is no use to him, and that he can get along better without it. I must confess that I never met this individual in the flesh, but I know that he exists in some of our manufacturing centres. As a species he is, however, doomed to extinction in the struggle with his competitors, and we may consider him out of court in the discussion of schemes of technical education. It is now generally admitted that the days of empiricism have passed away, and most manufacturers admit that present success and future development depend upon a proper recognition of technical, *i.e.* of applied, science. But unless the manufacturers themselves speak loudly on this question, the voices of those who wish to promote scientific education may be drowned by the clamour of mere theorists.

In no other department of our manufactures is the want of technical science more felt than in the chemical industries. We not only see this in the greater development of these industries abroad, but in some of our most successful factories here—and this applies more especially to the coal-tar colour industry—foreign chemists are employed, and, as I have lately been informed by a well-known manufacturer, it is even impossible to get the necessary plant properly made in this country. There is no

doubt that the recondite character of the truths of chemical science, as compared with the more obvious truths of mechanics and physics, has much to do with the want of popularity of this branch of knowledge, and is responsible for the circumstance that our science is regarded with comparative indifference until some branch of manufacture is *in extremis*. In our national characteristic of being "practical," we are apt to become short-sighted in our manufacturing policy, and to recognise only actualities to the exclusion of the potentiality conferred upon a nation by a broader scientific culture.

### DISCUSSION

Mr R. J. FRISWELL said, the great difficulty scientific men had to encounter was to persuade those whose money interest placed them at the head of large factories that scientific work, the practical outcome of which was not immediately visible, was really of value. It was a long struggle, but he thought they were beginning to see daylight at last. A feeling was beginning to be awakened, not in the coal-tar colour industry alone, but in others also, and he thought the coming generation of manufacturers would take to heart the lesson which Professor Meldola and others had so strongly enforced, so that in the course of a few years a great change would be seen in this direction. What had been said with regard to the alizarin industry showed that already in that direction a very marked change was beginning to take place, and he hoped it would not be many years before they saw a change in the same direction in other coal-tar colours. Every Englishman must feel that it was a great reproach to this country that an industry which originated here should so far have slipped out of her grasp.

The Chairman (Professor JAMES DEWAR) said he desired most heartily to thank Professor Meldola because he had not in any way feared to tell the whole truth. When such a statement came from a man who had not confined himself purely to the scientific side of the question, but who had been himself superior chemist in a large works, it showed that he was, from his thorough knowledge of both sides of the question, entitled to speak in this bold and straightforward way. He must differ from the writer of the paper on one point, where he said he had never met the manufacturer who declined to say that science was a great bene-

factor. On two occasions in his life he had certainly had this experience. At one time, when a young man, he was offered the same position that Professor Meldola held for several years, and the difficulty which arose was entirely with reference to supplying the laboratory. On another occasion a similar difficulty arose with a very distinguished man, in which he projected something of the same kind, but the moment he began to ask where the materials were, and where the laboratory was, the engagement was abruptly broken off, as this gentleman saw no reason for having a laboratory in connection with the work at all. There was the difference. It was not only the stimulus in the large German laboratories, where active research was going on, but it was the large stimulus now existent among the factories themselves. There the men were not isolated, but, as they had heard, there were something like fifty chemists in one large factory, so that there was a little scientific world in itself, where there was an incentive to continuous work. With reference to the question as to the want of popularity in chemical science, he admitted it, of course, but the question was, what was the full explanation of it? He thought it arose in a great degree from the want of encouragement of chemistry in the older universities. He said so, not because the older universities sent out a larger number of men than the young ones, but simply because up to the present time they had no such thing as even a creditable chemical laboratory. Although he held the chair in one of these universities, he was always ashamed if anyone asked to see the chemical laboratory, because, in truth, there was none. It was in the same condition as it was a century ago. If you got a pupil out of the mass who showed some originality, you found you could not retain him, you had not the materials or the money, and consequently he went to some large German laboratory where material was to be had, and where his work was encouraged. As long as that went on, how could the science be popular? Another important point in the paper was the proof of the marvellous result of action and reaction. Of course, as a physical principle, that was admitted on all hands to be an elementary truth, but all these facts now brought forward had had the most remarkable effect as a stimulus on the growth of the more recondite scientific investigation; every new success connected with any colour which might be discovered was a stimulus to further investigation, and the result was that all the marvellous group of colouring matters

were now to be had in such enormous quantity that the chemist got numerous new foci from which to start fresh investigations. Consequently, all this industry had conversely affected chemical laboratories, purely scientific, by the supply of splendid new material.

Mr LIGGINS said it was impossible to overestimate the brilliancy and beauty of these coal-tar dyes, or to give too much praise to those chemists who had invented the processes which had given such brilliant results, and as an artist he must say it was impossible, either with oil or water-colour, to produce colours of such beautiful shades as some of those which were exhibited; but there were two sides to every question, and several times within the last few weeks the most thorough condemnation of aniline dyes had been pronounced in that room by able men and scientific men, especially in connection with the artistic work of Japan and India. The carpets of India were said to be ruined by aniline colours which were used in dyeing, and it was said to be one of the greatest misfortunes for India that these colours had been introduced, as they were very inferior to those the natives had been for centuries in the habit of using; besides that, it was very commonly supposed that the colouring matters of various articles of clothing were poisonous.

Professor MELDOLA said, with regard to the fugitiveness of these colours, there was a great deal of misapprehension, and the same with regard to the poisonous character of the dyes. A great controversy had been carried on lately in Bradford before the Society of Dyers and Colourists. Specimens had been submitted to careful analysis, in order to detect arsenic, because it was known that some of these colours were made by means of arsenic acid, and it was thought they might retain traces which rendered them poisonous; but the amount found was infinitesimal. No doubt many of these colours were fugitive, but, on the other hand, some of the alizarin colours, which were used for dyeing carpet yarn, would bear exposure to light, and remain unaltered long after the old vegetable colours had faded completely away.

IX.: 1896

## THE ORIGIN OF THE COAL-TAR COLOUR INDUSTRY, AND THE CONTRIBUTIONS OF HOFMANN AND HIS PUPILS

By W. H. PERKIN, PH.D., D.C.L., F.R.S.

(Hofmann Memorial Lecture: *Journal of the Chemical Society*, 1896, p. 596)

THE illustrious man whose lifework we are called on to commemorate was well known to very many of us, especially those who had the privilege of being his students and assistants. We can all recall the pleasure and interest with which we listened to the lucid and graphic accounts of his researches which he used to bring before the Chemical Society in years gone by; and great was felt to be the loss, not only to us, but also to the country, when he left it for his fatherland: but now we mourn a far greater loss, and one which we realise more and more deeply as we consider the incidents of his remarkable career—a career of such incessant activity and brilliant achievement.

I am charged with a duty which I wish had been placed in more capable hands than mine: to give an account of the rise and progress of the coal-tar colour industry, and its relation to the Hofmann school; and, as being connected with its commencement, I am requested to make the account to a large extent autobiographical—a part of my task which it would have been more agreeable to me to have seen undertaken by others rather than myself.

This industry holds an unique position in the history of chemical industries, as it was entirely the outcome of scientific research. We have to go back to 1825, when Faraday discovered benzene, or, as he then termed it “bicarburetted hydrogen,” for the first investigation which clearly bears upon the subject.

Faraday separated the hydrocarbon from the liquid products condensed on compressing the gas obtained from oil. A year later (1826), Unverdorben obtained aniline by the mere distillation of indigo, and called it "crystalline." Runge afterwards obtained it from coal-tar oil, and having observed that it produced a violet-blue coloration with chloride of lime, called it "kyanol." It was subsequently obtained from indigo by Fritsche by distilling this colouring matter with caustic alkali. We then come to the important work of Mitscherlich, who obtained the hydrocarbon benzene from a new source, namely, benzoic acid,—whence the name, and produced from this nitrobenzene. Zinin subsequently found that *benzidam*, as he termed it, could be produced by the action of sulphuretted hydrogen in presence of ammonia on an alcoholic solution of nitrobenzene.

This brings us to the commencement of Hofmann's researches on aniline, a substance which he used sometimes to speak of as his "first love." In his first published paper he showed that Unverdorben's crystalline, Runge's kyanol, Fritsche's aniline, and Zinin's benzidam were all the same compound, for which he afterwards selected Fritsche's name, aniline. Later on, Hofmann and Muspratt prepared toluidine from toluene from tolu balsam.

The work on the separation of aniline from tar was done before the date of Hofmann's coming to this country, viz. in 1843. After his arrival here in 1845, he continued his researches, and, to realise something of his indomitable perseverance, it is necessary to remember that, until the coal-tar colour industry was established, practically all the aniline he used in his numerous inquiries was procured by the laborious and costly process of distilling indigo with potash.

In 1843, organic chemistry was still in its infancy, and coal-tar naphtha had not yet been investigated. Runge had isolated carbolic acid, pyrrol, kyanol or aniline, and leucol or quinoline. Naphthalene was well known to exist in tar, having been separated by Garden, as early as 1820. Dumas had discovered par-naphthalene or anthracene, and chrysene and pyrene had been referred to by Laurent, but these were very doubtful compounds. This was about all that was known of the composition of coal-tar at that time. Hofmann showed, in 1845, that benzene must exist in the naphtha, as he found that aniline could be produced from it, but he never separated this hydrocarbon; shortly afterwards, however, he induced his pupil, Charles Mansfield—of

whom he always spoke in the highest terms—to undertake the investigation of the liquid hydrocarbons of coal-tar.

On reading over the account of Mansfield's investigation, and bearing in mind that in those days fractional distillation was conducted in old-fashioned glass retorts with the thermometer in the liquid, it is impossible not to admire the patience and perseverance he exercised, as well as the systematic and skilful manner in which he worked.

All who have undertaken fractional distillations, even with all our present knowledge and improved apparatus, know how difficult it is to detect and isolate products in a mixture such as coal-tar naphtha. Yet Mansfield obtained benzene in a pure state, and toluene sufficiently so for Hofmann to prepare toluidine from it. He also obtained pseudocumene, and was led to believe in the existence of xylene. In describing his work, he modestly remarks :—

“It has been perhaps the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other which has deterred experienced chemists from devoting their time to disentangling the oils here treated off: and perhaps to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in” (*Jour. Chem. Soc.*, 1849, 1, 246).

Amongst the inquiries carried on by Hofmann, in the early days of the Royal College of Chemistry, were those classical “researches regarding the molecular constitution of the volatile organic bases,” in which he succeeded in displacing the hydrogen of the  $\text{NH}_2$  group by different alcohol radicles, eventually obtaining also the ammonium compounds. In the first of these (*Jour. Chem. Soc.*, 3, 1851) he describes ethylaniline (p. 284), and diethylaniline (p. 288), also methylaniline (p. 295). The method used in these researches, of substituting hydrogen in amines by means of the iodides and bromides of the alcohol radicles, and also the substituted anilines which were obtained, although not connected with the foundation of the coal-tar colour industry, have been of great value in its after development. These few references to observations on the early work carried on at the Royal College of Chemistry, for the sake of science *only*, show, in fact, what valuable material was produced for the coming new industry; indeed, without the research of Mansfield, it could never have become an industry.

The foregoing brings the work of the Royal College of Chemistry up to near the date when I became a student there ; and it will, perhaps, be well if I here refer to my young days, and state how it came to pass that I had the good fortune to study under Hofmann, especially as it will enable me to say a few words in reference to one of his old pupils, Mr Thomas Hall, B.A., who has done much for the cause of science.

As long ago as I can remember, the question of what pursuit I should follow was constantly before me. Even when very young, I interested myself in several subjects of a mechanical kind, and worked at them to the best of my ability ; and elementary as the experience then gained was, it had a lasting influence upon me. When I was between twelve and thirteen years of age, a young friend was good enough to show me some chemical experiments ; amongst these were some on crystallisation, which seemed to me most marvellous phenomena : as a result, my choice was fixed, and it became my desire to be a chemist, if possible, as I saw that there was in this science something far beyond the mechanical and other pursuits I had been previously occupied with. At this time I left the school I was attending, and entered the City of London School, of which Dr Mortimer was then head master. Here lectures were given on chemistry and natural philosophy ; indeed, I believe this was the first school in which experimental science was taught. The lecturer was one of the masters, Mr Thomas Hall, an old student of Hofmann's who had obtained all the chemical knowledge he possessed by working at the Royal College of Chemistry. To attend these lectures was a source of great pleasure to me. There was also a yearly examination in science, and the examiner was also one of Hofmann's pupils, and his first assistant, none other than my friend Mr, now Sir, Frederick Abel. In the City of London School I was consequently brought directly under Hofmannic influence, if I may so term it, for all who came in contact with those who worked with him had infused into them by induction his enthusiasm for chemistry. Mr Hall very soon took an interest in me, and installed me as one of his lecture assistants. Science, however, was not allowed to interfere with the ordinary school curriculum, so that the lectures, and the preparations for them, were delegated to the interval for dinner, and being very much interested in preparing the experiments, I not unfrequently found this interval had passed before I left off work ; but, fortunately, I never



found that the abstinence thus caused acted prejudicially upon me. Whilst with Mr Hall, I heard much of the Royal College of Chemistry and its Professor, and after my master had very kindly had several interviews with my father—who wished me to be an architect and not a chemist—it was my good fortune to be allowed to follow my bent, and go to the Royal College of Chemistry, in Oxford Street.

Before passing from my schooldays, I feel I must say a few more words about my old schoolmaster, to whose kindness I owe so much. Thomas Hall was a born teacher, who took an individual interest in his scholars, studying their characters, and stimulating any special qualities he saw they possessed, and, at the same time, inculcating the highest moral qualities. He hated anything that was mean or underhand, and, at the same time, was very genial and kind-hearted; this may be gathered from the fact that the boys used to speak of him as *Tommy Hall*. His influence on behalf of science, especially the science of chemistry, was great; it appears, from a list of old City of London School boys, kindly given me by Mr John Spiller, that more than thirty boys in whom he had taken an interest afterwards worked at the Royal College of Chemistry, and of these I may mention the following as having contributed papers to our *Transactions*:

J. J. Bowrey, J. T. Brown, Frank Clowes, W. H. Deering, Edward Divers, J. A. Newlands, F. J. M. Page, W. H. Perkin, Alexander Pedler, J. Spiller, and W. Thorp.

I entered the Royal College of Chemistry when I was in my fifteenth year, at the time when that institution became part of the School of Mines, but I only took up the study of chemistry. After seeing Dr Hofmann with my father, the first person I encountered in the laboratory was the Assistant, Mr W. Crookes, who set me to study the reactions of the metals.

There was no theatre at the Royal College then, and the students had to go to the Museum of Practical Geology in Jermyn Street to hear the lectures on chemistry, which involved a rather serious loss of time; but the lectures made up for this, as Hofmann spared no pains in making them as interesting, instructive, and perfect as he possibly could, illustrating, as far as practicable, everything by experiment, so that the facts were firmly impressed upon the mind. At that time he also had a very efficient lecture assistant, the late Mr Witt. Hofmann was good enough to let me attend these lectures a second time.

When going through the ordinary course of qualitative and quantitative analysis, the students working at research appeared to me to be superior beings, something beyond ordinary persons ; and being possessed with a desire to join their ranks, the ordinary course, and also gas analysis by Bunsen's method, was quickly gone through. Hofmann then set me to work at research, and very curiously gave me as a subject the hydrocarbon anthracene, or, as it was generally called in those days, paranaphthalene. To obtain this, pitch was taken as the starting-point, but as it was found that this method of preparation was a very tedious one to carry out in the laboratory, Hofmann kindly obtained some of the crude product for me from Mr Cliff, of Bethels Tar Works. As is well known, Hofmann—especially at that period—was much interested in the formation of organic bases from hydrocarbons, and the object of my investigation was to produce, if possible, a nitro compound, and then convert this into a base by reduction. However, anthracene refused to give a nitro compound, and consequently no base could be obtained, but, in the course of my work, I prepared the compound we now know as anthraquinone, and also the chlorine and bromine derivatives of anthracene. But these substances could not be got to yield intelligible results on analysis, and at that time it never occurred either to Hofmann or myself that there was any likelihood of Dumas and Laurent's formula for the hydrocarbon (*i.e.*  $C_{15}H_{12}$ ) being incorrect. The consequence was that this research was set aside, but I shall show further on that the experience I then gained was of great importance to me several years later, when I commenced to work at the production of alizarin.

Hofmann next set me to work to study the action of chloride of cyanogen on naphthylamine in the same way that he had examined the action of this gas on aniline. In those days there were no depots where pure products for research could be obtained as there now are, and for this inquiry even the naphthalene had to be purified in the laboratory ; this research was soon completed, but was not written out and published until nearly twelve months afterwards. It was brought before the Chemical Society when the meetings were held in Mr Pepper's house in Cavendish Square.

Hofmann had a marvellous power of stimulating his students, and of imparting to them his own enthusiasm ; he took the strongest personal interest in their work, visiting three or four times in the week even those who were going through the

reactions, while those engaged in research work were seen daily by him, and if anything of special interest was going on, more than once in the day. His power of directing research was also most remarkable; with the aid of a few watch-glasses, a glass rod, and a small gas flame he would make a number of experiments, and from the information thus gained tell his students how to proceed with their work. I well remember how one day, when the work was going on very satisfactorily with most of us and several new products had been obtained, he came up and commenced examining a product of the nitration of phenol which one of the students had obtained by steam distillation; taking a little of the substance in a watch-glass, he treated it with caustic alkali, and at once obtained a beautiful scarlet salt of what we now know to be orthonitrophenol. Several of us were standing by at the time, and, looking up at us in his characteristic and enthusiastic way, he at once exclaimed, "Gentlemen, new bodies are floating in the air." I mention this just as an example of the way in which he used to stimulate us by his own example.

After I had completed the research on the action of chloride of cyanogen on naphthylamine, Hofmann promoted me to the position of an assistant in his research laboratory; I was then seventeen years of age. Mr A. H. Church, now Professor Church, was among the assistants in the laboratory. This position proved most valuable to me.

At this time Professor Cahours came over from Paris to work with Hofmann on the allyl compounds, a research in which Professor Church and I had to assist. They then commenced their splendid work on the phosphorus bases, and I well remember the excitement and interest which prevailed when Paul Thénard's triethylphosphine was first produced by the action of zinc ethyl on phosphorus trichloride, and Hofmann's delight when he found it was vigorously acted on by methyl and also ethyl iodide, producing white, crystalline, phosphonium iodides. I was occupied with this research until I left the Royal College.

I may here refer to an incident which shows how greatly Hofmann was interested in his scientific work. One day, when he was going his usual rounds in the general laboratory, a student standing not far from him poured a quantity of concentrated sulphuric acid into a thick glass bottle he was holding in his hand, which contained a small quantity of water; the consequence was that the heat evolved caused it to crack and the bottom to fall

out. Some of the acid splashed up from the floor into Hofmann's eye, and we feared would have a permanently injurious effect upon it. Hofmann was sent home in a cab, and had to be kept in bed in a dark room during several weeks, his old friend, Dr Bence Jones, attending him. But during this time, and notwithstanding his sufferings, he was so anxious about his work that we used to have to visit him in his darkened bedroom, to report progress and also to receive any instructions he had to give.

Whilst in the research laboratory I had the privilege of meeting St Claire Deville, who came to London for the purpose of exhibiting specimens of sodium and aluminium at a lecture given by the Rev. T. Barlow at the Royal Institution, of which the lecturer was Secretary.

Whilst assistant under Hofmann, I had but little time for private work in the daytime ; as, however, I wished to continue research work, part of a room at home was fitted up as a rough laboratory, and there I was able to work in the evenings or during vacations. In this laboratory a research was carried on conjointly with Mr Church on some colouring matters derived from dinitrobenzene and dinitronaphthalene. One of the products we then obtained afterwards proved to be amidoazonaphthalene, or, as we called it, azodinaphthyldiamine. This appears to have been the first case of a definite compound being obtained of the azo class and shown to possess dyeing powers. As Dr Caro has referred to this in his notice in the *Berichte* of the late Peter Griess, I need not make any further observations on the subject here (*Ber.*, 1892, 25, 4, 1011).

At this period much interest was taken in the artificial formation of natural organic substances ; but at the time I was at the Royal College of Chemistry, although the theory of compound radicles, the doctrine of substitution, etc., were occupying much attention, very little was known of the internal structure of compounds and the conception as to the method by which one compound might be formed from another was necessarily very crude.

Thus, in the Report of the Royal College of Chemistry, published in 1849, Hofmann refers to the artificial formation of quinine as a great desideratum, and then states :—

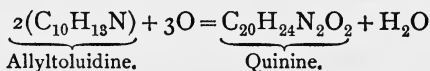
“It is a remarkable fact that naphthalene, the beautiful hydrocarbon of which immense quantities are annually produced in the manufacture of coal gas, when subjected to a series of chemical processes, may be converted into a crystalline alkaloid. This

substance, which has received the name of naphthalidine, contains 20 equivalents of carbon, 9 equivalents of hydrogen, and 1 equivalent of nitrogen." (C = 6. O = 8.)

"Now if we take 20 equivalents of carbon, 11 equivalents of hydrogen, 1 equivalent of nitrogen, and 2 equivalents of oxygen, as the composition of quinine, it will be obvious that naphthalidine, differing only by the elements of 2 equivalents of water, might pass into the former alkaloid simply by an assumption of water. We cannot, of course, expect to induce the water to enter merely by placing it in contact, but a happy experiment may attain this end by the discovery of an appropriate metamorphic process."

In fact there was but little other ground to work upon in many instances than this kind of speculation.

As a young chemist I was ambitious enough to wish to work on this subject of the artificial formation of natural organic compounds. Probably from reading the above remarks on the importance of forming quinine, I began to think how it might be accomplished, and was led by the then popular additive and subtractive method to the idea that it might be formed from toluidine by first adding to its composition  $C_3H_4$  by substituting allyl for hydrogen, thus forming allyltoluidine, and then removing 2 hydrogen atoms and adding 2 atoms of oxygen, thus



The allyltoluidine having been prepared by the action of allyl iodide on toluidine, was converted into a salt and treated with potassium dichromate; no quinine was formed, but only a dirty reddish-brown precipitate. Unpromising though this result was, I was interested in the action, and thought it desirable to treat a more simple base in the same manner. Aniline was selected, and its sulphate was treated with potassium dichromate; in this instance a black precipitate was obtained, and, on examination, this precipitate was found to contain the colouring matter since so well known as aniline purple or mauve, and by a number of other names. All these experiments were made during the Easter vacation of 1856 in my rough laboratory at home. Very soon after the discovery of this colouring matter, I found that it had the properties of a dye, and that it resisted the action of light remarkably well.

After the vacation, experiments were continued in the evenings when I had returned from the Royal College of Chemistry, and combustions were made of the colouring matter. I showed it to my friend Church, with whom I had been working, on his visiting my laboratory, and who, from his artistic tastes, had a great interest in colouring matters, and he thought it might be valuable and encouraged me to continue to work upon it; but its evident costliness and the difficulties of preparing aniline on the large scale, made the probability of its proving of practical value appear very doubtful. Through a friend, I then got an introduction to Messrs Pullar, of Perth, and sent them some specimens of dyed silk. On 12th June 1856, I received the following reply:—

“If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time. This colour is one which has been very much wanted in all classes of goods, and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you pattern of the best lilac we have on cotton—it is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests that yours does, and fades by exposure to air. On silk the colour has always been fugitive: it is done with cudbear or archil, and then blued to shade.”

This somewhat lengthy extract is quoted because it gives a glimpse at the state of the dyeing trade in reference to this shade of colour at that period.

This first report was very satisfactory; the “if” with which it commenced was, however, a doubtful point.

During the summer vacation, however, the preparation of the colouring matter on a very small, technical scale was undertaken, my brother (the late T. D. Perkin) assisting me in the operations, and, after preparing a few ounces of product, the results were thought sufficiently promising to make it desirable to patent the process for the preparation of this colouring matter. This was done on 26th August 1856 (Patent No. 1984). A visit was then made to Messrs Pullar’s, and experiments on cotton dyeing were made, but, as no suitable mordants were known for this colouring matter, only the pale shades of colour, produced by the natural affinity of the dye for the vegetable fibre, were obtained; these, however, were admired. Experiments on calico printing were also made at some print works, but fears were entertained that it

would be too dear, and, although it proved to be one of the most serviceable colours as regards fastness, yet the printers were not satisfied with it because it would not resist the action of chloride of lime like madder purple.

Although the results were not so encouraging as could be wished, I was persuaded of the importance of the colouring matter, and the result was that, in October, I sought an interview with my old master, Hofmann, and told him of the discovery of this dye, showing him patterns dyed with it, at the same time saying that as I was going to undertake its manufacture, I was sorry that I should have to leave the Royal College of Chemistry. At this he appeared much annoyed, and spoke in a very discouraging manner, making me feel that perhaps I might be taking a false step which might ruin my future prospects. I have sometimes thought that, appreciating the difficulties of producing such compounds as aniline and this colouring matter on the large scale, Hofmann perhaps anticipated that the undertaking would be a failure, and was sorry to think that I should be so foolish as to leave my scientific work for such an object, especially as I was then but a lad of eighteen years of age ; and I must confess that one of my great fears on entering into technical work was that it might prevent my continuing research work, but I determined that, as far as possible, this should not be the case.

Still, having faith in the results I had obtained, I left the College of Chemistry and continued my experiments, and found that not only aniline, but also toluidine, xyloidine, and cumidine gave a purple colouring matter when oxidised.

The following is a copy of the principal part of the complete specification of the patent I took out at this time :—

### DYEING FABRICS

“The nature of my invention consists in producing a new colouring matter for dyeing with a lilac or purple colour stuffs of silk, cotton, wool, and other materials in the manner following :—

“I take a cold solution of sulphate of aniline, or a cold solution of sulphate of toluidine, or a cold solution of sulphate of xyloidine, or a cold solution of sulphate of cumidine, or a mixture of any one of such solutions with any others or other of them, and as much of a cold solution of a soluble bichromate as

contains base enough to convert the sulphuric acid in any of the above-mentioned solutions into a neutral sulphate. I then mix the solutions and allow them to stand for 10 or 12 hours, when the mixture will consist of a black powder and a solution of a neutral sulphate. I then throw this mixture upon a fine filter, and wash it with water till free from the neutral sulphate. I then dry the substance thus obtained at a temperature of  $100^{\circ}$  C., or  $212^{\circ}$  F., and digest it repeatedly with coal-tar naphtha, until it is free from a brown substance which is extracted by the naphtha. Any other substance than coal-tar naphtha may be used in which the brown substance is soluble and the colouring matter is not soluble. I then free the residue from the naphtha by evaporation, and digest it with methylated spirit, or any other liquid in which the colouring matter is soluble, which dissolves out the new colouring matter. I then separate the methylated spirit from the colouring matter by distillation, at a temperature of  $100^{\circ}$  C. or  $212^{\circ}$  F."

Fresh quantities of colouring matter were prepared and taken to Scotland, and, although the method of applying it by means of lacterin (casein) was then found to give very good results, yet the printers who tried it did not show any great enthusiasm; and even Messrs Pullar began to fluctuate in their opinion as to the advisability of erecting plant for its manufacture, and wrote:—"Should it appear that it will not be of service to printers, it will be questionable whether it would be wise to erect works for the quantity dyers alone will require." In January 1867, Mr R. Pullar, however, advised me to see Mr Thos. Keith, a silk dyer of Bethnal Green, London, and, after making a few experiments with the colouring matter, and exposing the specimens he dyed to the light for some time, he was much pleased with the result, and encouraged me to go on with its production.

I was then joined in the undertaking by my father—who was a builder, and had sufficient faith in the project to risk the necessary capital—and also by my brother, who also had a good knowledge of building, and, as he had taken part in the preliminary experiments on the preparation of the dye, his assistance proved most valuable, especially as he was possessed of good business capabilities. Plans were prepared and a site obtained at Greenford Green, near Harrow, and in June 1857 the building of the works was commenced.



At this time, neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be, as the kind of apparatus required and the character of the operations to be performed were so entirely different from any in use that there was but little to copy from.

In commencing this manufacture, it was absolutely necessary to proceed tentatively, as most of the operations required new kinds of apparatus to be devised and tried before more could be ordered to carry out the work on any scale.

But the mechanical were not the only difficulties. Benzene at this time was only made to a very limited extent, as there was but little use for it, and it was only after making several inquiries that it was ascertained where it could be obtained. That used at first came from Messrs Miller & Co., of Glasgow. It was also of very unequal quality, and required refractionating before use; its price was 5s. per gallon. No nitric acid sufficiently strong for the preparation of nitrobenzene could be obtained commercially, and, as we did not want to complicate our works by manufacturing the substance, experiments were made with a mixture of sodium nitrate and sulphuric acid, using the latter in rather larger proportions than necessary to give an acid sodium sulphate. This method was found to succeed on the small scale, but, when working with large quantities, special apparatus had to be devised, and a great many precautions had to be taken to regulate the operation; however, very large quantities of nitrobenzene were made by it. Nitrobenzene had never been prepared in iron vessels before this time.

It was only three years before the works were started that Béchamp had made the interesting discovery that finely divided iron and acetic acid were capable of converting nitrobenzene into aniline; had it not been for this discovery, the coal-tar colour industry could not have been started. To carry this process out on the large scale, special apparatus was also required, and, on account of the energy of the action which takes place, special precautions had to be adopted; but no great difficulties were encountered in this operation. Potassium bichromate at that date fluctuated between 9½d. and 11d. per lb., and was therefore a costly product.

Many more details might be gone into in reference to the

difficulties to be contended against at the starting of the industry, but sufficient has been said to give some idea of them ; however, in less than six months after the building of the works was commenced, namely, in December 1857, aniline purple, or Tyrian purple, as it at first was called, was in use for silk dyeing in Mr Keith's dye-house.

But in dyeing large quantities of silk, difficulties were again encountered, on account of the great affinity of the colouring matter for the fibre causing unevenness, and some time was taken up in experimenting on this subject, until eventually it was found that by dyeing in a soap bath a very pure and even colour could be produced. This process was afterwards found to be the most suitable for dyeing silk with magenta, Hofmann's violet, and many other colouring matters.

Aniline purple having now been proved to be an important colouring matter, which could be produced on a manufacturing scale, it attracted much attention, and, as a consequence, many others commenced its manufacture, and began to experiment with aniline, especially in France ; all kinds of oxidising agents were used, but potassium dichromate still proved to be the best, the next best being chloride of copper, the use of which was patented by Dale and Caro, in 1860.

The French manufacturers were not long before they succeeded in producing the colouring matter (the French patent being invalid, owing to a mistake as to the date it was necessary to take it out in reference to that of the English patent), and in using it in dyeing their goods, both silk and cotton. The calico printers of this country then began to be alive to the necessity of following them, and this made the demand for the aniline purple—which the French now began to call mauve—so great that, notwithstanding the continued increase which had been taking place in the works at Greenford Green, it could not be kept pace with. At this time, a very beautiful archil colour had been produced by Messrs Guinon, Marnas, & Bonnet, called French purple ; this also was applied to calico printing, and the printers in this country who could not get a supply of aniline purple used this until their requirements could be met. A little before this, Mr Pullar and I separately discovered a process for mordanting cotton, so that it could be dyed with aniline purple to any depth of colour, and thus it became of much more value to the cotton dyer than it was so long as its natural affinity for the

fibre could alone be relied upon. The process consisted in the use of tannin and a metallic oxide.

For calico printing, the colouring matter was first applied in combination with lacterin, albumin, or gluten, but endeavours were soon made to find some new method by which these might be dispensed with, and I worked for some considerable time on this subject at the Dalmonach Print Works, Alexandria, Dumbartonshire, where the colour was first practically used for printing in this country. I devised a process, which consisted in printing on a lead salt, converting this into a salt containing a fatty acid by means of soap, and then dyeing in a soap bath containing the colouring matter; the fatty lead salt then took up the colouring matter, whilst the soap prevented the white from being stained; this process was patented by myself and Mr Mathew Grey. It produced beautiful shades of colour, but could not be used where combinations with other colours were required, and therefore did not prove useful.

Printers then experimented on the use of tannin and a metallic oxide, the process used in cotton dyeing devised by Mr Pullar and myself; a modified form of this process has become the most important used. Another process was also very largely used, patented by M. Schultz and myself, which consisted in forming an insoluble arsenite of alumina and colouring matter on the fibre, the colours produced in this way being very brilliant, as well as fast to washing. Before the aniline purple could be introduced for dyeing woollen and mixed fabrics, some weeks were also spent at Bradford in finding out suitable methods of applying it.

Thus it will be seen that, in the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but, owing to the fact that it belonged to a new class of dyestuffs, a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, etc. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all the colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, etc.

All this time a host of experimentalists continued making trials with aniline and all kinds of chemicals, and early in 1859,

three years after the discovery of aniline purple, or mauve, M. Verguin discovered fuchsine, also called magenta and roseine, and, later on, rosaniline by Hofmann.

From what has been said above, it will be seen that the discovery of this colouring matter was made under more favourable auspices than that of mauve: everything was ready for its production and application, it was also an easier product to manufacture and relatively to the aniline used was formed in much larger quantities than mauve was, but it was not nearly so fast against light, and when first experimented with I thought this would have been very detrimental to its extensive use, remembering the experience that I had gone through with mauve; but things had changed, and the love of brilliancy had begun to outrun the regard for durability, indeed, as is well known, magenta has proved to be one of the most successful of the coal-tar colours ever discovered. M. Verguin's process was a very remarkable one, and it has never transpired whether he was led to it by any scientific reasoning or not; it will be remembered that it consists in heating commercial aniline and anhydrous tetrachloride of tin nearly up to the boiling-point of the mixture; it was first carried out by Messrs Reynard Bros., of Lyons.

We were thus indebted to France for the second step in the coal-tar colour industry. Soon other processes were invented for the production of magenta, but the most practical one, after M. Verguin's, was that in which mercury nitrate was used; large quantities of colouring matter were made by this method.

The fuchsine, or magenta, first made in France, was but very imperfectly purified, and a good deal of that afterwards made in Germany simply consisted of the "melt" produced by heating aniline with mercury nitrate.

Being naturally interested in this new colouring matter, I made many experiments with it, and in a lecture I delivered before this Society, on 16th May 1861 (*Jour. Chem. Soc.*, 1862, 14, 230) (when I was honoured by the presence of Michael Faraday), an account of some of the results obtained by its examination was given, in which it was shown that it was the salt of an organic base (a fact at that time believed in by some, but doubted by others) precipitated by alkalis and at the same time dissolved by them to some extent, yielding colourless solutions, and that its nitrate could be obtained in the form of octahedra, having

a beautiful green metallic reflection ; this was the first occasion, I believe, on which it was described as a crystalline compound. Attention was also called to the fact that its salts could not contain oxygen, which was afterwards confirmed by Hofmann ; and it was further pointed out that other products were formed along with it, one possessing an orange colour (chrysaniline), and another a purple colour (violaniline, mauvaniline, etc.).

In speaking of the manufacture of rosaniline in this country, I must first refer to another of Hofmann's pupils, Edward Chambers Nicholson, of the firm of Simpson, Maule & Nicholson, who brought the manufacture of this compound to a state of perfection which, I believe, has not been surpassed—so far as purity is concerned—up to the present time.

It is of interest to trace the manner in which Messrs Simpson, Maule & Nicholson became connected with the coal-tar colour industry. They were originally manufacturers of fine chemicals, etc. When aniline purple was found to be successful, and was exciting a great deal of interest, this and other firms were anxious to manufacture it, and consequently wished to have a licence for the purpose, but no agreement could be come to. They were then very desirous of manufacturing nitrobenzene for our use in producing aniline. At first they could not do this at a sufficiently low price, but eventually succeeded in producing it cheaply enough to make it worth our while to supplement our own make by theirs, as the demand for aniline purple was then so rapidly increasing. In this way they soon became considerable producers of nitrobenzene ; they then set to work to prepare aniline, which after a time they succeeded in doing. In this manner they leisurely, as it were, became fully prepared to go a step further, and become manufacturers of colouring matters.

Dr David Price at this time joined the firm, and Nicholson and he apparently experimented with the products he had patented in 1859, namely violin, purpurin, and roseine, obtained by oxidising aniline with lead peroxide ; these colouring matters, however, were not found to be of practical value. They then turned their attention to the newly discovered colouring matter, fuchsine. This they commenced manufacturing, giving it the name of one of Dr Price's products, roseine.

H. Medlock, another of Hofmann's pupils at the Royal College of Chemistry, took out a patent on 18th January 1860, for the production of magenta, by heating aniline with arsenic

acid ; eight days later, Nicholson filed a similar patent, but did not proceed with it when he learnt what Medlock had done. Medlock's patent is notorious for the amount of litigation that arose owing to the occurrence in it of the word "anhydrous." The formation of magenta by the use of arsenic acid proved in the hands of Nicholson, and also of others, a great improvement on the previous processes, and for a long time was *the* process for the production of this colouring matter, until, in fact, it was superseded by the use of nitrobenzene instead of arsenic acid.

One of the things Hofmann used to impress on those of his students who were engaged at research work was the great importance of preparing their products in as nearly pure a condition as possible—especially those which were to be submitted to analysis ; some of us used to think that we should get as good results by examining the substances when crystallised fewer times than he required, especially when the products were difficult to obtain and the quantities became smaller and smaller on each recrystallisation ; but he was right. Nicholson, when at the Royal College, made several investigations under Hofmann's direction, studying the compounds of phosphoric acid with aniline ; the formation of cumidine from cumene from cuminic acid ; also caffeine and some of its compounds ; and, in conjunction with F. A. Abel, he investigated strychnine. He also appears to have been an adept at combustions, as he made the combustion of benzene for Mansfield ; his name appearing also in de la Rue's paper on cochineal as having made one of the combustions of nitrococcusic acid. There is no doubt that Hofmann's teaching as to the importance of working with pure materials was strongly impressed upon Nicholson when carrying on these researches, and that it greatly influenced him when he became engaged in the manufacture of colouring matters. It is only right to add that Dr D. Price, with whom he was for some time associated in this industry, and whom I knew when at the Royal College of Chemistry as a most thorough, painstaking, and careful worker, would also second his efforts in this respect. I may also add that I feel sure Hofmann's influence in this direction had also a considerable influence on my own after-career as a chemist.

At first Messrs Simpson, Maule & Nicholson supplied magenta, or roseine, as they called it, to the dyers in alcoholic solution, but afterwards, when they had obtained it in a pure

condition, they sold it in crystals (usually the oxalate). In their process of purification they boiled the crude solution of the colouring matter with milk of lime, and collected the base which deposited from the clear solution thus obtained, and from this prepared the desired salts.

By this time the coal-tar colour industry had become one of no mean dimensions in this country, and also in France, and it was quickly developing in Germany and elsewhere. The number of colours was also increasing, for not only had mauve or aniline purple and fuchsine been discovered, but Girard and De Laire had made their remarkable discovery of imperial violet and blue de Lyon by heating aniline with fuchsine, thereby—as is now known—phenylating this colouring matter.

When first speaking of fuchsine, I mentioned that it was discovered by M. Verguin, and, from a practical point of view, this may be considered correct. Nevertheless it appears to have been first seen as far back as 1856, when Natanson (*Annalen der Chemie und Pharmacie*, 1856, 98, 297) observed that in heating aniline and chloride of ethylene in a sealed tube to 200° C., the mixture becomes of a rich blood-red colour; Hofmann also, in 1858, when acting on aniline with carbon tetrachloride, obtained, besides carbotriphenyltri-amine, a small quantity of this substance as a secondary product, which he describes as “a very soluble substance of a magnificent crimson colour.”<sup>1</sup>

In the Report of the Exhibition of 1862 (Class II., sec. A, p. 126), Hofmann, in speaking of the discovery of this colouring matter, says:—“It may be said to have been discovered at two different times according as the question is considered from a scientific or industrial point of view;” and at p. 126:—“Industrially, the discovery of aniline red was made by Messrs Verguin and Renard Brothers of Lyons.”

The investigation Hofmann made with the Nicholson products soon set at rest the conflicting views which at first existed in reference to this colouring matter, and proved that it was a

<sup>1</sup> About two years after M. Verguin's discovery of fuchsine, the use of carbon tetrachloride and aniline as a means of preparing this colouring matter was tried, for reasons connected with patent rights, by MM. Monnet and Drury of Lyons. They first employed a temperature of 116°–118° C. until the reaction between these two substances was over, and then heated the product up to 170° or 180° C. By this means of working, they apparently obtained a larger yield than Hofmann, but the process never became a practical one. See *Moniteur Scientifique*, t. iii., 15th January 1861.

well-defined triamine—which he renamed rosaniline—forming salts free from oxygen. He then regarded the base, which had the formula  $C_{20}H_{21}N_3O$ , as a hydrate of the anhydrous compound  $C_{20}H_{19}N_3$ . Hofmann examined many of the salts of rosaniline—those with one molecule of acid, the ordinary salts used in dyeing, and the hydrochloride with 3 mols. of acid. He also obtained the interesting compound, leucaniline, by treating rosaniline with reducing agents, a compound which has its representation in all triphenylmethane colouring matters. The investigation is a memorable one, as being the first investigation which gave correct information respecting the formula of a coal-tar colouring matter.

It had been observed by manufacturers that some varieties of aniline yield much more rosaniline than others, samples boiling at temperatures much higher than the boiling-point of the pure compound being found particularly adapted for the production of the red; and it appears that Nicholson had ascertained that pure aniline was incapable of yielding rosaniline. Hofmann studied this subject, using aniline prepared from indigo and from pure benzene, and his experiments confirmed Nicholson's. The idea then naturally suggested itself, that the toluidine contained in commercial aniline might be the source of the colouring matter. But, on making experiments with toluidine (orthotoluidine was not then known) it was found that this base also was incapable of producing the dyestuff; on taking a mixture of aniline and toluidine, however, it was at once produced in quantity, showing that both bases were necessary for its production (Report, International Exhibition, 1862, Class II., sec. A, p. 130).

This discovery was of great importance and interest, and explained most of the facts connected with the use of anilines of different boiling-points. In the case of mauveine, this discovery was not of so great importance as in the case of rosaniline, because pure aniline yields a purple colouring matter (pseudomauveine), as well as mixtures of aniline and toluidine.

Mauve had also been obtained in a pure crystallised condition, but technically this was not found of much advantage, as the colours obtained with it in this condition were only slightly superior to those obtained with the less expensive precipitated colouring matter which was usually supplied to the consumer.

Having examined aniline red or rosaniline, Hofmann was also desirous of investigating aniline purple or mauve, but when he



spoke to me on the subject, the colouring matter was already under investigation in my own laboratory.

The crystallised aniline purple sent into the market was the acetate of the base to which I gave the name mauveine. This base is remarkable for its stability and tinctorial power. Its investigation (*Proc. Roy. Soc.*, 1864, 12, 713) showed that it possesses the formula  $C_{27}H_{24}N_4$ , and that, unlike rosaniline, it is not a hydroxy compound. Moreover, the base is a strongly coloured compound of a blue-violet colour. When treated with reducing agents, it yields a leuco compound, but this is so sensitive to the action of oxygen that on exposure to the air it instantly changes back to mauveine. Its ordinary salts are produced from 1 mol. of base and 1 mol. of acid. From a more recent research on this colouring matter (*Jour. Chem. Soc.*, 1879, 717), I have shown that a dihydrochloride and corresponding platinum salt can be obtained, and the characteristic changes which a solution of this substance in concentrated sulphuric acid undergoes on dilution, namely, from a dull green to a blue, and lastly to a purple, show that probably salts formed by the union of mauveine with more than 2 mols. of acid exist. The ordinary commercial product has also been shown to consist of two colouring matters, one forming very soluble and apparently uncrystallisable salts called pseudomauveine, having the formula  $C_{24}H_{20}N_4$ , and produced from pure aniline; the other forming less soluble and beautifully crystalline salts of the formula  $C_{27}H_{24}N_4$ , derived from paratoluidine and aniline. This colouring matter, unlike rosaniline, does not freely undergo changes with reagents on account of its great stability, so that few derivatives have been obtained from it serving to elucidate its constitution, which is still unknown.

Messrs Simpson, Maule & Nicholson, after engaging in the manufacture of rosaniline for some time, undertook that of Girard and De Laire's imperial violet and bleu de Lyon, obtained by heating a salt of rosaniline with aniline (Pat., January 1861).

Mr Nicholson spent much time in studying the conditions most favourable to the production of these compounds, especially the blue, so as to obtain it in a pure condition, and in this he was very successful. This was due to his knowledge of the importance of using pure materials in its manufacture. The rosaniline base he used was not merely the best he produced for the preparation of rosaniline salts, but he purified it much further

by means of methylated spirit ; the aniline was prepared for the purpose from the purest benzene he could obtain ; he also paid much attention to the selection of the best acid to use in combination with rosaniline, and found that weak organic acids, such as acetic and benzoic acids, were the most suitable. In this way he eventually obtained the blue in a condition of purification unequalled by others.

Provided with the purified blue by Nicholson, Hofmann soon discovered that the base had the formula  $C_{38}H_{33}N_3O$  ; this he regarded as a hydrate of the compound  $C_{38}H_{31}N_3$ , of which he obtained a hydrochloride of the composition  $C_{38}H_{31}N_3HCl$ . The blue was converted by reducing agents into a leuco compound.

As far back as 1850 (*Phil. Trans.*, 1, 93, *Jour. Chem. Soc.*, 3, 283), when engaged in his researches on the molecular constitution of the volatile organic bases, Hofmann had endeavoured to displace the hydrogen in aniline by phenyl, by heating it with phenol, but was unsuccessful ; we can, therefore, easily understand his delight when he found that on boiling rosaniline with aniline the colouring matter became phenylated. The long-desired method of effecting the displacement of hydrogen by phenyl had, in fact, been discovered, and we find that no sooner had he recognised that the blue was a triphenylosaniline than he telegraphed the result to Paris.<sup>1</sup> The *Comptes rendus* of the sitting of the Academy of 18th May 1863 contains the following note :—

“ M. Le Secrétaire Perpétuel communique une Courte Note de M. Hofmann conçue dans les termes suivants.

“ Bleu d’Aniline.—En poursuivant mes recherches sur les couleurs d’aniline, je suis arrivé à un résultat très simple ; le bleu d’aniline est la rosaniline triphénylique : une molécule de rosaniline et trois molécules d’aniline renferment les éléments d’une molécule de bleu d’aniline et trois molécules d’ammoniaque.”

The paper, communicating fuller details of his results on this colouring matter, was read on 6th July of the same year (*Compt. rend.*, 1863, 57, 25). Speaking in this paper of Nicholson, he pays him this tribute : “ That in him was united the genius of the manufacturer and the habits of a scientific investigator.”

<sup>1</sup> Hofmann had made the discovery apparently on the same day, for Professor McLeod, who was his assistant at that time, gives me an entry from his diary dated 18th May 1863, which runs thus : “ The doctor told me that he had made a fine discovery, and that aniline blue is the triphenylated rosaniline. Rosaniline,  $C_{20}H_{19}N_3H_2O$  ; aniline blue,  $C_{20}H_{16}(C_6H_5)_3N_3H_2O$ .”

We find the discovery of the phenylation of rosaniline afterwards bearing fresh fruit in the hands of De Laire, Girard, and Chapoteaut, who established the remarkable fact that when boiled with its own hydrochloride, aniline acted in a similar manner, producing diphenylamine and ammonia; by using aniline hydrochloride and toluidine, they, in like manner, obtained phenyltoluylamine (*Compt. rend.*, 1866, 63, 91).

Aniline blue having proved to be triphenylrosaniline, it was soon seen that the different shades of violet imperial were rosanilines more or less phenylated.

Nicholson also found that, on heating acetate of rosaniline to  $200^{\circ}$ – $215^{\circ}$  C., ammonia was disengaged, and a purple colouring matter produced, which he called regina purple. This substance was found to be a monophenylrosaniline (patented 20th January 1862).

One of the great obstacles in the way of the application of aniline blue was its slight solubility in water, which rendered the dyeing operations unsatisfactory; this also militated against its use in calico printing for some time (the most suitable process for its use for this purpose first found being that of Schultz and myself with arsenate of alumina, but with this long steaming and afterwards clearing in a soap bath was required; the colours thus obtained, however, were very pure and very durable). Nicholson naturally was very desirous of overcoming this obstacle, and no doubt the well-known process of rendering indigo soluble by dissolving it in sulphuric acid, and thus converting it into a sulphonic acid, occurred to him; at any rate, by experimenting in this direction, he succeeded in obtaining the desired result and patented the process (1st June 1862). Nicholson obtained two sulphonic acids—a mono and a tri—the first being known as Nicholson's blue, and the latter as soluble blue, and it is owing to the discovery of these derivatives of aniline blue or triphenylrosaniline that this colouring matter became of such importance.

This method of treating aniline blue was very interesting as being the first instance of sulphonating an aniline colour, a process which of late years has become of so much importance, not only in rendering difficultly soluble dyes soluble, but also in changing the chemical nature of the colouring matters, and thus extending their applications as dyes, as in the case of rosaniline sulphonic acid.

It was Nicholson who succeeded in isolating the yellow or

orange colouring matter which is formed in the manufacture of rosaniline; he prepared it in a pure state, and called it phosphine. Hofmann undertook the examination of this dye, and showed that it is represented by the formula  $C_{20}H_{17}N_3$ , differing from that of rosaniline in containing 2 atoms of hydrogen less; the base is capable of forming salts with 1 or 2 molecules of hydrochloric acid, the nitrate being remarkable for its insolubility.

After discovering that aniline blue or bleu de Lyon was a triphenylrosaniline, Hofmann was very naturally inclined to experiment on rosaniline with the agents he had used so successfully in his experiments on the molecular constitution of the volatile organic bases, namely, the haloid compounds of the alcohol radicles, to see what influence these radicles would have if introduced into the base: he found that they had, like phenyl, though not to the same extent, a blueing effect, the colour changing from red to purple, and then to violet as the hydrogen atoms were gradually displaced, colouring matters being produced which were found to be of great beauty when applied to silk, etc. In his first paper on these products (*Compt. rend.*, 1863, 57, 30), he gives an account of the action of methyl, ethyl, and amyl iodides on rosaniline, and amongst the products he obtained at that time describes the highest ethylated derivative he had succeeded in producing as the iodethylate of triethylrosaniline,  $C_{20}H_{16}(C_2H_5)_3N_3 \cdot C_2H_5I$ .

He patented the method of producing these colouring matters on 22nd May 1863.

It is easy to see how Hofmann was led to the production of these compounds in the regular sequence of his work, but it is curious that E. Kopp had evidently prepared some of them as long back as 1861. E. Kopp remarks in his paper in the *Comptes rendus*, 1861, 52, 363, "I have only stated in my notice these substitutions as a hypothesis, but their existence is very real; I have already obtained some of them, and it is a remarkable thing that the red shade disappears, and is converted into a violet, becoming bluer and bluer as the hydrogen is displaced by the hydrocarbons." It appears that he sent some specimens of his products to M. Dumas.

When Hofmann patented the use of methyl, ethyl, and amyl iodides for the preparation of these colouring matters, it seemed almost incredible that substances such as these, which had

hitherto only been used in research, should be employed in the manufacture of a dye ; but such circumstances have constantly arisen in the history of this remarkable industry—aniline itself, the parent of artificial colours, being an example—and nothing now appears to be too rare or difficult to prepare, to be used in its development.

It is difficult to understand why E. Kopp did not go on with his work on these substitution compounds, unless it was owing to the fact that rosaniline was expensive in his days, and he considered the alcoholic haloids too costly to employ for practical purposes.

The Hofmann violets were the most brilliant in colour of any which had been produced, and proved not to be so costly as might be anticipated, as the iodine from the ethyl iodide used could be mostly recovered ; but these colouring matters have not the stability of mauve or imperial violet, and at first it was thought that their use would be limited, but the increasing desire for brilliancy was still superseding that for stability, and the result was, that these colouring matters were very largely used, and interfered very considerably with the sale of the mauve and imperial violets, except for pale shades of colour, when, unless the colouring matter used be stable, the goods fade so quickly as to be of little value.

The products formed on heating mauveine salts with aniline apparently are not comparable with those obtained from rosaniline, and although the product becomes bluer no ammonia is evolved ; from my later experiments, it seems most likely that the aniline used takes no part in the change, the blueing being a change in the colouring matter, the consequence of the temperature employed.

When treated with ethyl iodide, mauveine behaves unlike rosaniline, yielding a beautiful colouring matter, which is of a redder shade, and not bluer as in the latter case. This colouring matter, called dahlia (patented on 6th November 1863), consists of a monethylic derivative of mauveine, its hydrochloride being represented by the formula  $C_{27}H_{23}(C_2H_5)N_4HCl$ . No further change is effected by ethyl iodide, and it is uncertain whether the product is a substitution or an addition compound (it may be remarked here that at times some quantity of a dark, blue-black, almost insoluble substance containing iodine is also produced).

This dahlia or ethylmauveine was used by the calico printers and dyers to some extent, though not largely, on account of its costliness. It is, however, a colouring matter which gives shades of very considerable stability on exposure to light.

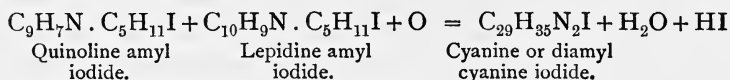
The discovery that the introduction of such radicles as phenyl or ethyl altered the colour of rosaniline so greatly, made it of interest to see whether other kinds of hydrocarbon groups could be introduced to modify its tint. Amongst other products, brominated turpentine was used, and on heating it with rosaniline hydrochloride dissolved in methylated spirit or methyl alcohol under pressure, it was found that a very beautiful purple or violet colouring matter could be produced; the process was patented in 1864, and large quantities of a colouring matter, known as Britannia violet, were prepared in this manner. At first it was thought that the hydrocarbon radicle of the brominated turpentine entered the rosaniline, but it now appears most probable that the product consisted of methylrosanilines produced by the action of methyl bromide formed from hydrogen bromide resulting from the decomposition of the bromo compound. The colouring matter was more soluble than Hofmann's ethyl violet, but I could not succeed in crystallising it, and, therefore, it was not subjected to analysis.

When the base of Britannia violet is acted on by acetyl chloride, two products are obtained, namely, a violet colouring matter much bluer in shade than the original violet, and a bluish-green compound. The base of this latter has a very feeble affinity for acids, and does not combine with acetic acid, whilst the base of the violet compound does so freely, and in virtue of these different properties the two colouring matters are easily separated. The green dye proved to be of practical value, and considerable quantities of it were prepared for the calico printers. It was known as Perkin's green, but after a time it was displaced by iodine green. It has not hitherto been investigated. For its manufacture, large quantities of terchloride of phosphorus were prepared, from which and acetic acid large quantities of acetyl chloride were made—another instance of the use of a research reagent on the large scale.

The last investigation relating to colouring matters carried out by Hofmann in this country was that of the very interesting substance known as quinoline blue, discovered by Greville Williams, of which the latter gave an account in the *Chemical News* for

11th October 1860 (p. 219). A beautiful specimen of the crystallised substance was displayed in the exhibition of 1862 under the name of cyanin. Quinoline blue was a very pure shade of colour, and, although an expensive product, attempts were made to introduce it as a dye; unfortunately, although produced from bases of remarkable stability, it was very fugitive, goods dyed with it fading very quickly indeed when exposed to the light—its sensitiveness being so great that on placing it under a glass positive photograph and exposing to sunlight, after only a short time a quinoline blue positive picture was produced.

Hofmann separated from quinoline two blue compounds, to one of which he gave the formula  $C_{30}H_{39}N_2I$ , and to the other the formula  $C_{28}H_{35}N_2I$ . According to later researches, the blue is a condensation product derived from quinoline amyliodide and lepidine amyliodide.



This formula differs from that given by Hofmann to one of the products he examined by an atom of carbon only.

After I left the Royal College of Chemistry, the researches on the phosphorus bases in which I had been helping were continued by Drs Leibius and Holzmann, to whose able assistance Hofmann refers in one of his papers; but in carrying out the part of this work relating to the phosphammonium, phospharsonium, and arsammonium compounds, another assistant was active, who is referred to by Hofmann in the following words:—

“I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr Peter Griess has assisted me in the performance of my experiments on the phosphorus bases. The truly philosophical spirit in which this talented chemist has accompanied me through the varying fortunes of this inquiry, will always be one of my pleasing recollections.”

We know how the high opinion thus expressed by Hofmann of Griess not only lasted, but became enhanced as time went on; and although Griess was not one of Hofmann's pupils, I cannot refrain from thus referring to him here, as several of his most important early researches on the diazo compounds were made within the walls of the Royal College of Chemistry, thereby connecting this Institution with work which of late years has had

such a marvellous influence on the development of the coal-tar colour industry. But it is not my intention, nor indeed is it necessary for me, to go into the history of the diazo compounds, as this has been so very ably done by my friend Caro in his memoir of Peter Griess, whom he held in such high esteem, and who was also one of his greatest friends.

Hofmann's departure was not only a cause of regret to those who had worked under him and to all his friends; it was a heavy loss also to the country at large, as no one had ever done so much for the cause of chemical science in the kingdom as Hofmann did, nor had anyone exercised to such an extent that wonderful power he possessed of stimulating the enthusiasm of his students and of inciting in them a love of chemistry and of scientific research. His success is especially striking when the early history of the Royal College of Chemistry is taken into account—especially its financial difficulties, the dissatisfaction of some of the subscribers, and the want of understanding as to the value of scientific research shown both by them and the public at large. When all these circumstances are considered, we cannot but marvel at the courage and indomitable determination he displayed, which enabled him to overcome all difficulties and to persevere in maintaining the high standard of teaching he adopted at the beginning, as well as to continue the prosecution of scientific research for its own sake.

Notwithstanding the immense amount of work Hofmann must have had to attend to in connection with the building and fitting up of the new chemical laboratories of the Frederick William University of Berlin, which took place during the first four years after he left England, namely, from May 1865 to May 1869, no break occurred in his scientific activity, each year producing accounts of fresh work accomplished. It was not, however, until 1869 that he published anything fresh in connection with the coal-tar colours, but in this year several communications appeared.

Having found that the production of rosaniline depended on the presence of two bases, aniline and toluidine, he naturally carried his investigation of the subject further, and experimented with xyloidine (meta). However, on heating this base with oxidising agents, either alone or in presence of toluidine, no colouring matter was obtained; but when it was heated with pure aniline, a red was formed, which he called xyloidine red, which was supposed



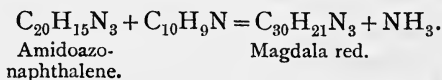
to be a homologue of rosaniline, probably of the composition  $C_{22}H_{25}N_3O$ . The colour produced on wool and silk by this dyestuff was almost as bright as that of rosaniline itself (*Ber.*, 2, 377). In a second paper relating to this subject, published in conjunction with Martius (*Ber.*, 2, 411), an account is given of similar experiments with an isomer of xylidine, amidoethylbenzene, which, from the more recent researches of Beilstein and Kühlberg (*Zeitsch. f. Chem.* [2], 5, 524), we now know must have been a mixture of the ortho and para compounds. No red colouring matter was formed from this on boiling it with an oxidising agent, either alone or mixed with toluidine or even with aniline, thus affording proof of the interesting fact that an ethyl group cannot take the place of a methyl group in the interaction which is involved in the production of colouring matters of the rosaniline class.

After the discovery of mauve and magenta, many experiments were made with  $\alpha$ -naphthylamine, as a source of colouring matter, and a variety of products was obtained and patented; but it is unnecessary for me to enter into an account of these here, as most of them were found to be of no technical value. I may, however, allude to two naphthalene derivatives which have proved useful; the first of these, naphthazarin, was discovered by Roussin in 1861, who thought it was artificial alizarin. This beautiful substance, which is now known to be a dihydroxy- $\beta$ -naphthoquinone, lay dormant for a long time, but, owing to the discovery of improved methods of producing it, has of late come into use for dyeing black on wool. The second was discovered by Martius, and is known as "Martius yellow" or dinitro- $\alpha$ -naphthol. These were the principal colouring matters derived from naphthalene known prior to 1867, when Schiendl discovered the naphthalene red now known by the name of Magdala red, a substance remarkable for the beautiful fluorescence of its solution. The original process for its preparation consisted in heating naphthylamine, acetic acid, and potassium nitrite together, and then adding more naphthylamine and again heating until the desired colouring matter was produced.

Hofmann investigated this red, and assigned to it the formula  $C_{30}H_{21}N_3$  (*Ber.*, 1869, 2, 374).

As this colouring matter and the above formula appeared to be related to an old friend of mine, azodinaphthylidiamine (amidoazonaphthalene), I made it the subject of experiments,

and found that it was easily produced on heating amidoazonaphthalene with an acid and naphthylamine, an action taking place which it was thought involved the displacement of an atom of hydrogen by naphthyl and the formation of ammonia :



The colouring matter was called azotrinaphthyldiamine (*Proc. Roy. Inst.*, 14th May 1869).

In a second paper, published in July of the same year, on the nature of naphthalene red, Hofmann confirms my observations (*Ber.*, 2, 413).

It has since been shown, however, by Julius (*Ber.*, 1886, 19, 1365), that the action which occurs when amidoazonaphthalene is treated with naphthylamine is not nearly so simple as above indicated, and that the formula of the hydrochloride of Magdala red is  $\text{C}_{30}\text{H}_{21}\text{N}_4\text{Cl}$ , not  $\text{C}_{30}\text{H}_{22}\text{N}_3\text{Cl}$ .

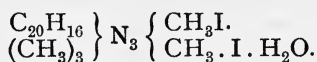
The research on Magdala red led Hofmann to study the compound produced by the action of aniline on amidoazobenzene, a substance described by Martius and Griess, but discovered by Dale and Caro in 1863, and called by them induline. The examination of this product was afterwards continued by Hofmann in conjunction with Geyger, under the heading of colouring matters obtained from aromatic azodiamines, and published in 1872 (*Ber.*, 5, 472). They called this substance azodiphenyl blue, and showed that its hydrochloride had the formula  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{Cl}$ .

In 1869 Hofmann also continued his researches on chrys-aniline, studying the action of methyl and ethyl iodide on the base ; he obtained trimethyl and triethyl substitution products (*Ber.*, 2, 378).

In preparing Hofmann violet, it was found that on precipitating the colouring matter from its aqueous solution by means of sodium chloride, a certain quantity of a bluish-green product remained in solution which could not be separated (though improved in colour) by the addition of sodium carbonate ; this was precipitated by means of picric acid, and as it proved to be a valuable green dye, it, after a time, was supplied in small quantities to dyers under the name of iodine green. It was then found by J. Keisser (French patent, 18th April 1866) that the colouring matter could be obtained in much larger quantities by

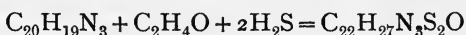
methylating rosaniline, dissolved in methyl alcohol, with methyl iodide, the operation being completed at a comparatively low temperature, and eventually it was obtained in a pure crystallised state. This substance being evidently related to the methyl-rosanilines, Hofmann was naturally interested in it, and with Girard undertook its investigation (*Ber.*, 2, 440).

The results they obtained, on analysing the iodo compound, led them to represent it by the formula



They found that this compound decomposes when heated at the temperature of boiling water for a few hours, and instantly at  $130^\circ$ – $150^\circ$  C., becoming changed into a violet colouring matter; in fact, it behaves like an ammonium or addition product. As the complicated history of the methyl and ethyl derivatives developed, it was found that the formula above given required to be modified to some extent; but this is in no way surprising, as it is practically impossible by analysis alone to arrive at a true conclusion as to the constitution of a compound of such high molecular weight, so unstable and so difficult to obtain pure.

Another green dyestuff to which Hofmann directed his attention at this time was aldehyde green, produced by the action of aldehyde on rosaniline in presence of sulphuric acid, whereby a blue colouring matter is formed, which is transformed into the green by the action of an aqueous solution of sodium thio-sulphate. Lauth, apparently, was the first to produce the blue compound, in 1861, by subjecting a solution of rosaniline in alcohol, methyl alcohol, acetic acid, or acetone to the action of zinc chloride and other metallic salts, but the conversion of the blue into the green was accomplished by Cherpin in 1862. This was the first aniline green dye discovered (emeraldine, which was of no value, excepted), and was much used. Hofmann showed that aldehyde green contained sulphur, and assigned to it the composition indicated by the formula  $\text{C}_{22}\text{H}_{27}\text{N}_3\text{S}_2\text{O}$ , representing its formation by the following equation,



(*Ber.*, 1870, 3, 761).

The next researches it will be most convenient to refer to, though not quite the next as to date, are those on the methyl

violets ; but, before considering these it may be mentioned that, in continuation of his researches on rosaniline derivatives, Hofmann, in 1873 (*Ber.*, 6, 263), examined the violet obtained by Hobrecker by the action of benzyl chloride and methyl iodide on a solution of rosaniline in methyl alcohol, assigning to it the formula  $C_{20}H_{16}(C_7H_7)_3N_3CH_3I$ .

Until long after the commencement of the coal-tar colour industry, chemists and experimenters directed their attention chiefly to aniline as a source of colouring matter ; but in 1861 Lauth made some experiments on the product Hofmann obtained by acting with methyl iodide on aniline, which he described as methylaniline (*Jour. Chem. Soc.*, 1851, 3, 296), but which recent researches have shown is a mixture of methylaniline and dimethylaniline, and by oxidising this he obtained violet colouring matters. Writing of these in 1867, Lauth says (*Laboratory*, 1867, 138), "The violets obtained from methylaniline possess a richness and purity which leave nothing to be desired. . . . Nevertheless, they were not adopted by manufacturers, who, indeed, at the time mentioned (1861) attached less importance to the beauty of a colour than to its permanence. In this latter respect the methylaniline violets do not excel, and, consequently, dyers would have nothing to do with them. Gradually, however, people have become accustomed to colours which fade on exposure to the solar rays. . . . Accordingly, two years after the experiment made by myself, Dr Hofmann succeeded in introducing these results."

These remarks confirm those already made in reference to the gradual change in public opinion which led to the disregard of permanency in favour of brilliancy of colour.

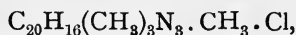
Lauth further remarks that Hofmann's method of producing these colouring matters is the inverse of that proposed by him ; the aniline being first converted into rosaniline and then methylated, whilst in his case this operation is first performed on the aniline.

It would, however, not have been practicable to carry out this process if the aniline had to be methylated with methyl iodide, because the base thus prepared would be too expensive to use as the raw material for the preparation of colouring matters. On account of the success of the Hofmann violet, experiments were made in France with the object of preparing methylaniline by a different and more economical process, so as to commercially produce Lauth's violet, and this was at that time

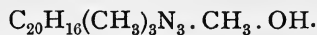
considered especially desirable by some manufacturers, because the production of rosaniline in France was the monopoly of one house, and, therefore, derivatives of this colouring matter could not be economically made by others.

Eventually a successful process was discovered by M. Bardy, chemist to the firm of Poirrier & Chapat, which consists in heating a mixture of aniline hydrochloride and methyl alcohol in a closed vessel to a high temperature. As is now well known, though not at first recognised, this process yields a mixture of mono- and di-methylaniline, consisting chiefly of the latter. Large quantities of methylated aniline were soon produced by this process, and used in the preparation of a violet colouring matter which was manufactured by Messrs Poirrier & Chapat, and called by them violet de Paris; a large block of this, weighing about 150 kilos, was exhibited in the Paris Exhibition of 1867. The question then arose as to whether violet de Paris was identical or isomeric with methylrosaniline violet. Lauth considered that it was isomeric, and remarks: "Hofmann violets consist of methylated and ethylated rosaniline, and rosaniline is derived from a molecule of aniline and two molecules of toluidine. The violet de Paris, on the contrary, is produced from pure aniline free from toluidine, transformed into methylaniline, which is isomeric with toluidine. This methylaniline when oxidised is converted into the violet, which may have a composition analogous to that of methylated rosaniline, but must differ from the latter in the same manner as methylaniline differs from toluidine."

Hofmann, being naturally interested in the relationship of these colouring matters, investigated the subject, and published his results in 1873 (*Ber.*, 6, 352). He first studied the conditions under which the colouring matter could be formed, showing that violet could be produced from pure dimethylaniline obtained by the distillation of trimethylammonium hydrate; he also came to the conclusion from the examination of the colouring matter that it was a methylchlorhydrate of trimethylrosaniline:—



the base being



He prepared iodine green by methylating this compound; also its leuco compound.

This research must have been a very difficult and laborious piece of work, and although Hofmann's views as to the constitution of the dimethylaniline violet are not those now accepted, the accuracy of his work has not been impugned.

The long controversy which arose, soon after the time when Hofmann published his constitutional formula of rosaniline, as to the constitution of this colouring matter, belongs to another chapter, and need not be referred to here.

Mention has already been made of the process for methylating aniline discovered by Bardy, which consisted in heating this base with hydrochloric acid and methyl alcohol. In 1871 Hofmann and Martius (*Ber.*, 4, 742) made some experiments in reference to this method, working at higher temperatures than those usually employed ( $280^{\circ}$ – $300^{\circ}$  C.), and continuing the heating for a considerable time; in this way they obtained, besides methyl, and dimethylaniline, a quantity of basic oil of higher boiling-point, which eventually proved to be a complex mixture of methylated homologues of dimethylaniline, the products of an intramolecular change or atomic wandering.

These remarkable researches, like so many other purely scientific discoveries, ere many years had passed, were found to be of technical value in connection with the coal-tar colour industry, the cumidine that is so extensively used in the preparation of some of the diazo colours being made by the method of Hofmann and Martius by heating xyloidine with hydrochloric acid and methyl alcohol to a high temperature, about  $300^{\circ}$  C.

Reverting once more to the early days of the coal-tar colour industry, I may now mention that the liquors from which mauve was precipitated were found to contain a red colouring matter which I succeeded in separating, although the amount obtainable was very small. This proved to be a beautiful dye producing crimson-red shades on silk. It was afterwards discovered that it could be produced by the oxidation of mauveine, and it was prepared in considerable quantity in this way, but was a very expensive product, and therefore not very largely used. This dyestuff was known first as "aniline pink," and afterwards as "safranine." In 1865 a colouring matter having the properties of safranine was produced without the use of mauveine by F. Duprey, by heating commercial aniline dissolved in acetic acid with lead nitrate. It was then obtained by acting on commercial aniline with nitrous acid and oxidising the mixture with arsenic

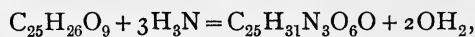
acid. The colouring matter prepared in this way was examined by Hofmann and Geyger (*Ber.*, 1872, 5, 531). They found it to be a base forming crystalline salts, among others a hydrochloride having the composition  $C_{21}H_{21}N_4Cl$ . As they found that it could not be produced from either aniline or paratoluidine, or a mixture of the two, but from orthotoluidine, they regarded it as a toluidine derivative. They also observed that the formula above given differs from that of mauveine by  $C_6H_4$ , making it appear possible that mauveine was phenylsafranine. In the course of an investigation of the safranine, obtained by the oxidation of mauveine, of which I published an account some time after this (*Jour. Chem. Soc.*, 1879, 35, 728), this substance was shown to form a hydrochloride represented by the formula  $C_{20}H_{18}N_4$ , which differs from that of the substance examined by Hofmann and Geyger by  $CH_2$ . On examining a commercial product manufactured by Messrs Guinon & Co., of Lyons, from commercial aniline, both substances were found to be present, showing that two "safranines" existed, and I then also showed that probably a third was formed by the oxidation of pseudo-mauveine.

The formula of the safranine hydrochloride obtained from mauveine will be seen from the above to differ from mauveine by  $C_7H_6$ , so that the relationship of these substances is probably not of so simple a character as Hofmann and Geyger supposed, though, of course,  $C_7H_6$  may simply mean displacement of hydrogen by tolyl. No doubt a great similarity exists between them, one proof of which is that their behaviour with sulphuric acid is analogous. This applies both to those referred to above and to the third compound since discovered.

In 1875 Hofmann made an examination of eosin (*Ber.*, 8, 62), and thus disclosed to the world an important manufacturing secret, proving to demonstration the impossibility in these days of long hiding from chemists the nature of any substance, however complex. Eosin, as is well known, was the first representative of a new class of colouring matters which has since become of great importance.

Chrysoidine, which may fairly be termed the parent of an even more important class of colouring matters, the azo dyes, the introduction of which marks a new era in this branch of chemistry, was investigated and publicly proclaimed by Hofmann in 1877 (*Ber.*, 10, 213).

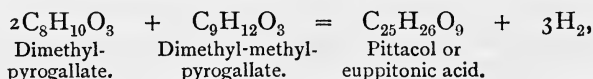
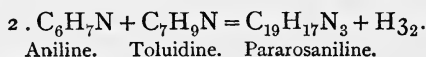
The colouring matter to which he next directed his attention was pittacal, also called euppitonic acid, the interesting compound discovered by Reichenbach, as far back as 1835, produced from wood tar. Hofmann (*Ber.*, 1878, 11, 1655; 1879, 12, 1371 and 2216) was led to regard this substance as hexamethoxyrosolic acid,  $C_{19}H_8(OCH_3)_6O_3$ ; on treating it with ammonia, he obtained a beautiful blue dyestuff, thus,



which he regarded as hexamethoxypararosaniline,



He then made the interesting discovery that the formation of pittacal, or euppitonic acid, from dimethylpyrogallate and dimethyl-methylpyrogallate took place in a manner analogous to that in which pararosaniline was formed, thus,



a comparison which is of considerable interest.

Hofmann's last research in connection with the coal-tar colour industry was made as late as 1887, and related to the quinoline red prepared by Jacobson, in 1882, from coal-tar quinoline, benzotrichloride, and zinc chloride. Hofmann, however, found that a better yield of colouring matter, either identical or isomeric with Jacobson's, is obtained by using a mixture of isoquinoline and quinaldine. Like quinoline blue or cyanine, the colour is not a fast one, which as previously mentioned, is remarkable, considering the stability of quinoline itself. It is a somewhat remarkable coincidence that this should have been the last research Hofmann made on the coal-tar colours, as quinoline (or leuconine) was one of the two substances he gave an account of in his first investigation published in 1843, when thirty years of age.

Excepting what is said of pittacal, and the brief reference to eosin and chrysoidine, the foregoing account has reference only to what may be termed aniline colours, the great chapter dealing with the history of technical chemistry, with which Hofmann's name is indissolubly linked.



An entirely new chapter in coal-tar chemistry opens in 1868, when Graebe and Liebermann (in connection with their researches on quinones) made their great discovery of the artificial formation of alizarin from anthracene. They patented their process in Germany in October, and in this country on 18th December of that year. Their process, it is well known, consisted in producing dibromanthraquinone, either by brominating anthraquinone in sealed tubes, or by oxidising tetrabromanthracene, and subsequently displacing bromine by hydroxyl, by fusion with alkali.

This discovery for the first time of a method of obtaining a vegetable colouring matter artificially was, however, as it stood, of no practical value, as such a process could not be carried out on a large scale.

But why should this be mentioned here? It may seem that any reference to the alizarin industry is out of place in a notice designed to elucidate Hofmann's influence on the development of our knowledge of products derived from coal-tar, as he apparently never took any part in the investigation of anthracene derivatives. Yet it is to his influence that I can trace back my interest in the subject, for, as mentioned early in this account, the very first subject in research which he suggested to me was to prepare a nitro compound and a base from anthracene. In the course of this work I not only became thoroughly acquainted with this hydrocarbon, but also prepared anthraquinone and other derivatives of it, and consequently was, perhaps, more fully prepared than any other chemist of the day to appreciate the discovery of the relationship of alizarin to anthracene, and was naturally impelled at once to attempt to adapt it to practical requirements. It is more than probable that I should have paid but ordinary attention to Graebe and Liebermann's work had I not possessed an early attachment to anthracene, and I am glad to recognise that I owe this to the knowledge and insight of my great master.

Being aware of the importance of alizarin as a colouring matter, and having some quantity of anthracene and anthraquinone left over from my experiments at the Royal College of Chemistry, I commenced to experiment on the formation of this substance, with the object of finding a process by which bromine might be dispensed with.

I knew of the remarkable stability of anthraquinone : that

it could be crystallised from concentrated sulphuric acid without undergoing change, and that in making a combustion of it, if the operation were at all hurried, part of the anthraquinone would pass through the heated tube, and condense at the cool end unaltered.

Moreover, not long before I commenced to work at the artificial formation of alizarin, namely, in 1867, Würtz and Kekulé had shown that when benzenesulphonic acid was heated with potassium hydrate, it gave a phenate and sulphite; and Dusart had also found that naphthalenedisulphonic acid was in like manner converted into a dihydroxynaphthalene; so that it appeared probable that if a disulphonic acid of anthraquinone could be obtained, it would be possible to convert it by the new reaction into alizarin.

Anthraquinone was therefore heated with oil of vitriol more and more strongly, until the boiling-point was nearly reached, as I was determined either to obtain a sulphonic acid or destroy the anthraquinone; and at last it was found that the anthraquinone had disappeared, yielding a product which was soluble in water. After the excess of sulphuric acid had been removed in the usual way with barium carbonate, the product was fused with caustic alkali, and to my delight it changed first to violet, and then became black from the intensity of its colour. On dissolving the melt, a beautiful purple solution was obtained, which gave a yellow precipitate when acidified, and on examination this was found to dye mordanted cloth like garancine.

On the 20th of May (1869) I sent dyed patterns to my friend Mr Robert Hogg, of Glasgow, who had a very large experience in reference to madder and garancine, and also of the coal-tar colours from the days of the mauve dye, whose opinion I valued very much in all practical matters connected with dye-stuffs, especially from a commercial point of view, and he was very favourably impressed with the results I had obtained. This process, however, was not patented until 26th June. (About the same time as I discovered this process, Graebe, Liebermann, and Caro quite independently arrived at the same result in Germany.) This process has proved the most permanently important one yet discovered, and is the one still universally used. I was also fortunate enough to discover a second process, which was of great value in the early days of the industry, but is not in use now so far as I know. It consisted in the use of

dichloranthracene as the starting-point, instead of anthraquinone. This substance was found to readily afford a sulphonic acid, which could be easily changed into anthraquinonesulphonic acid, either by oxidising its solution with manganese dioxide or more simply by heating it with sulphuric acid. This process was patented in November 1869.

After discovering processes by which artificial alizarin could be produced, the technical value of the artificially prepared dye-stuff had to be ascertained. Experiments were soon made by the calico printers, as no new processes had to be discovered for the application of this colouring matter, those in use for madder and garancine being suitable. Turkey-red dyers also experimented with it, but some were not so successful as others, for reasons easily understood afterwards, when the properties of anthrapurpurin, which it contained, were better known.

The subject of price, however, was the important question, because this product had to compete with those already in the market, namely, madder and garancine, and therefore high prices could not be obtained as in the case of a new dye.

Before this could be settled, the first thing necessary was to get a supply of anthracene. This substance was not at this date separated by the tar distillers, there being no use for it ; many of them, in fact, knew nothing of its existence, and the question as to whether it could be obtained in sufficient quantity and at a sufficiently low price had to be settled.

But experiments I had made on the small scale, on the distillation of soft pitch, at the Royal College of Chemistry, gave me confidence, and my brother and I entered into the matter with great energy.<sup>1</sup> At first we prepared anthracene by distilling pitch ourselves, and thought of using this as a source of this hydrocarbon on an extensive scale, as we felt it was capable of yielding a considerable supply. We knew, however, that it could also be obtained from the last runnings of the tar stills, from which it crystallised on cooling. My brother, therefore, visited nearly all the tar works in the kingdom, and showed the distillers how to separate the anthracene, promising to take all they could make, and in this way a sufficient and rapidly increasing supply for our requirements was soon obtained of all sorts of qualities, some being not much thicker than pea soup, from the

<sup>1</sup> My father, to whose great kindness I was so much indebted, died in 1864, so that our firm then consisted only of my brother and myself.

imperfect way in which it was drained. Very few tar distillers in those days had hydraulic presses, such as are now used, with which they could free the solid from the excess of oil. The value of the anthracene was estimated by washing with carbon bisulphide, afterwards alcohol was used, but for our own purposes we all along used an anthraquinone test. This method was afterwards worked out more perfectly on the Continent, and made a practical test for both the buyer and seller; but at the time I am writing of tar distillers were not sufficiently educated in such matters to use any but very simple tests.

The purification of the anthracene sufficiently for our purpose had then to be worked out, and in doing this I found out a curious fact, namely, that when distilled with caustic potash it was much improved in quality—considerably more so than when distilled either alone or with caustic soda. And potash-distilled anthracene was especially necessary when dichloranthracene had to be prepared, as it yielded a well-crystallised, easily purified product, whereas anthracene which had been distilled, either alone or with caustic soda, gave a badly crystallised, sticky product, which was very difficult to purify.

On examining into the action of caustic potash on anthracene, it was found that if, after the anthracene had been distilled off, the residue was freed from alkali by washing, and then distilled, a substance very like anthracene was obtained, which Graebe subsequently found to be the nitrogenous compound now known as carbazol. It is by means of caustic potash that this substance is now separated from crude anthracene, and the process is still used to a large extent to improve the quality of anthracene. All the anthracene we used at Greenford Green was treated in this manner.

The purification of the anthraquinone was at first effected by sublimation, followed by crystallisation. A good deal of difficulty was experienced in the conversion of this substance into its sulphonc acid, however, and at the high temperature at which combination took place, the formation of steam from the water produced at the same time led to considerable quantities of the anthraquinone becoming sublimed, which, although not lost, yet was a source of trouble in various ways. The means of overcoming this difficulty was to use fuming sulphuric acid, with which anthraquinone combined at a much lower temperature, but the only acid of the kind then made was the old-fashioned Nord-

hausen acid. We imported a quantity of this, and, of course, found it to work satisfactorily, but the difficulties and expense connected with the carriage and transport of this substance on account of its dangerous nature—supplied as it then was in large earthenware bottles—made it unsuitable for use in this country.

The artificial alizarin we first made was produced by the anthraquinone process, the method still used for its manufacture, but the difficulty in preparing the sulphonic acid in those early days just referred to caused us to turn our attention to the second process I had discovered, in which dichloranthracene was used. After finding out the best way of preparing the substance, our difficulties in reference to the sulphonic acid vanished, as dichloranthracene dissolves easily in hot ordinary oil of vitriol, producing dichloranthracenedisulphonic acid; on continued heating this acid oxidises, hydrogen chloride and sulphur dioxide being evolved and anthraquinonedisulphonic acid formed. Without this process, the manufacture of artificial alizarin in this country could not have been carried on with much success in the early days of its manufacture.

The conversion of the anthraquinonesulphonic acids into colouring matter by treatment with caustic alkali at a high temperature at first presented many difficulties when carried out on the large scale. Our earliest experiments were made by heating the mixture in iron trays in a large air bath. Mixtures of caustic potash and caustic soda were also experimented with instead of caustic soda alone. Then the mixture was placed in a revolving cylinder, heated in an air bath, small cannon balls being put into the cylinder to mix the product. But all these methods were only partially successful, the percentage of colouring matter produced not being so high as it should have been. At last heating in a very strong iron boiler under pressure was resorted to, and by adopting this method—which is now that universally used—we obtained a satisfactory result.

From the experiments we made in 1869 we felt pretty confident that artificial alizarin could be made at a price to compete with madder and garancine, and before the end of the year we had produced 1 ton of this colouring matter in the form of paste, in 1870 40 tons, and in 1871 220 tons, and so on in increasing quantities year by year.

The colouring matter produced from dichloranthracene was chiefly anthrapurpurin containing a little flavopurpurin. Theo-

retically it should have consisted of these products only, but owing to the occurrence of a secondary action, which I need not refer to here (see *Lectures Soc. Arts*, 30th May 1879), it also contained alizarin, which we sometimes separated when required for dyeing purples. This colouring matter yielded a shade of colour which answered most of the requirements of the consumers for some time, as it was chiefly used by the Turkey-red dyers, and the supply being limited, it was often used in combination with garancine, as in this way more brilliant reds could be obtained than when using garancine alone, though, of course, the use of the artificial colouring matter alone yielded still clearer and more fiery shades.

Dichloranthracene was afterwards found to yield a monosulphonic acid when treated with sulphuric acid, provided the temperature was kept low and the amount of acid limited; and when oxidised with manganese peroxide or other oxidising agent, this yielded anthraquinonemonosulphonic acid, from which alizarin alone could be obtained. But the properties of dichloranthracene-monosulphonic acid were such, and the technical difficulties of carrying out the process so considerable, that it was never used very successfully. Moreover, by this time, fuming sulphuric acid had come into use, and anthraquinonemonosulphonic acid could be more readily produced directly from anthraquinone. As we had been successful in producing artificial alizarin, others did not run much risk in following our lead; yet, up to the end of 1870, the Greenford Green Works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country.

From the foregoing, it is seen that, as in the case of the aniline colours, all the pioneering work connected with the foundation and establishment of this branch of the coal-tar colour industry was done in this country.

For the due development of this industry, it was necessary not only to attend to technical processes, but also to carry on scientific research in connection with it. Early in 1870, I had the honour of bringing before this Society an account of some experiments on the formation of the colouring matter obtained from the sulphonic acids of anthraquinone, showing that it contained alizarin possessed of both the chemical and optical

properties of that obtained from madder-root. At the same time, attention was directed to the existence of a second colouring matter, yielding reds more scarlet and purples of a bluer shade than alizarin (*Jour. Chem. Soc.*, 1870, 23, 133). This second colouring matter was afterwards made the subject of further investigation, and shown to be an isomer of purpurin; it was therefore called anthrapurpurin (*Jour. Chem. Soc.*, 1872, 25, 659, and 1873, 26, 425). Dichlor- and dibrom-anthracene and their disulphonic acids, etc., were also investigated. Anthraflavic acid, discovered by Schunck in some secondary products sent to him from my works, was made the subject of two researches; in the first of these, this compound was shown to be an isomer of alizarin, and not to contain  $C_{15}$  as supposed by its discoverer. In the second, the sublimed acid was examined and found to be identical with the unsublimed; it was also shown that when fused with alkali it did not yield alizarin, as stated by Schunck, but a colouring matter yielding orange-red colours with alumina mordants. This, Schunck and Roemer, some time afterwards showed to be another isomer of purpurin which was named by them flavopurpurin.

In this investigation, anthraflavic acid was found to yield a diacetyl and dibenzoyl derivative, which was evidence that it contained two hydroxyl groups like alizarin (*Jour. Chem. Soc.*, 1873, 26, 19). Later on, an investigation was made on the formation of anthrapurpurin, proving that, as in the case of flavopurpurin, the formation of the colouring matter from the disulphonic acid of anthraquinone is preceded by that of a dihydroxy derivative, also an isomer of alizarin, now known as isoanthraflavic acid, which, when heated with caustic alkali, is partially oxidised into anthrapurpurin and partially reduced (*Jour. Chem. Soc.*, 1876, i. 29, 851). Besides these, the formation of bromalizarin (*Jour. Chem. Soc.*, 1874, 27, 401), of  $\beta$ -nitroalizarin (*Jour. Chem. Soc.*, 1876, ii. 30, 578), of anthrapurpuramide (*Jour. Chem. Soc.*, 1878, 33, 216), and of the dibromanthraquinones discovered by Graebe and Liebermann and the colouring matters obtainable from them, were investigated (*Jour. Chem. Soc.*, 1880, 37, 554). Much work has also been done in reference to this industry by Graebe and Liebermann and other investigators.

The manufacture of artificial alizarin in Germany has been almost entirely confined to the anthraquinone process, fuming sulphuric acid being used in the preparation of the sulphonic

acids. For this purpose very strong acid, containing about 40 per cent. of anhydride, was made from Nordhausen acid, and used until the process of making sulphuric anhydride by decomposing sulphuric acid into sulphurous oxide, oxygen, and water, and recombining the two former, was introduced.

After being engaged in the coal-tar colour industry for eighteen years, my connection with it, technically, came to an end in 1874, when the alizarin industry had been well established and was rapidly extending.

On looking back over the period, it is of interest to see the wonderful progress the industry had made up to that time—a progress which was going on by leaps and bounds. I have no statistics connected with the precise period, but four years afterwards, namely in 1878—with the kind assistance of Dr Caro—an estimate of the value of the colours produced during that year was obtained, at a time when the industry had just passed its majority and was twenty-two years old. The sum amounted to £3,150,000. (See *Jour. Soc. Arts*, 30th May 1879.) Of its present position, it is very difficult to speak. Certainly its progress has been very great since 1878; but chiefly owing to the scientific skill bestowed upon the production of the colouring matters, their cost has been greatly diminished, so that I understand rosaniline hydrochloride, which once was worth about £3, 3s. per ounce, may now be purchased at 2s. 9d. per lb., and aniline at less than 6d. per lb. . . .

During the early days of the coal-tar colour industry, the complaint was made that the prosecution of purely scientific chemistry was being injured by its influence, as chemists were everywhere experimenting with aniline and other products, with objects of a more selfish than scientific character. It is probable that there was some truth in this for a time, but it was not long before a welcome change set in, and the work carried on in relation to this industry was soon conducted in a scientific spirit, even when the result sought for was expected to be of technical, as well as where it was expected to be of scientific, value. But the amount of work carried on from the latter point of view increased more and more, as interesting questions connected with the colouring matters and the methods by which they were produced presented themselves to chemists, and now if we look back and consider what has been accomplished, we find that this industry has directly and indirectly had a most marvellous



influence on the advancement of chemical science, especially that part of it relating to the aromatic series of compounds. No other industry in existence can at all be compared with it from this point of view. This has arisen from a variety of circumstances, one of which is that it has not been carried on by the rule-of-thumb method which has been so common in other cases. Again, as it has utilised the discoveries of chemists, it has handed back to them in return new products which they could not have obtained without its aid, and these have served as materials for still more advanced work : this kind of exchange, indeed, has been going on so repeatedly, that products formerly of the rarest and most complex character are now quite common substances in the coal-tar colour works.

We knew that aniline was at first a rare substance, and when it was afterwards proposed to use ethyl and methyl iodides in the preparation of ordinary dyestuffs, it seemed incredible that such substances could be introduced for such a purpose as already mentioned, substances which were but rarely met with even in chemical laboratories : but what are these compared with the substances now in use ?—their names would be too numerous to mention. One of the most striking facts connected with this industry is the remarkably rapid way in which it has utilised new discoveries which have often been no sooner made than they have been practically applied. This no doubt arises from the fact that an ever-increasing army of highly trained and highly gifted chemists are engaged in the industry, especially on the Continent, provided with splendid laboratories, libraries of scientific works, and all the most advanced appliances required in scientific research ; and the members of this army are not only making discoveries themselves and applying them, but are always on the alert to make the discoveries of others subservient to the industry.

As I have already mentioned, when this industry was first instituted, organic chemistry was comparatively in its infancy, especially if we regard it from our present standpoint. Kekulé had not then brought forward his remarkable benzene theory, and after he had done so its bearings required much elucidation before their importance was well understood. Only solid toluidine was known, orthotoluidine not having been discovered, although it was constantly present in the high boiling aniline used in making rosaniline ; but now the facts connected with

the ortho-, meta-, and para-position in substances containing the benzene nucleus, or of the  $\alpha$ - and  $\beta$ -positions in the naphthalene series, are among the most important to be considered in the manufacture of colouring matters ; in fact, this industry has done more to accentuate the importance and character of these positions than any other kind of experimental work.

Although at the commencement of the industry a good deal of work of a purely experimental character had to be done, nevertheless, from the first it was carried out on scientific lines, and this characteristic increased very rapidly, as is seen by the early date at which mauve and magenta were obtained in the pure crystallised condition : it was at this period, as previously stated, that Hofmann commenced his researches on rosaniline and its derivatives, and on other colouring matters, and these researches, taken with those of others, bear out the observations which have just been made. In looking over the work of Hofmann in this field, all who have had experience in the investigation of the subjects he undertook must realise that they presented no ordinary difficulties, especially as for some time he had nothing to guide him in his conclusions but the analytical results. In the early days of organic chemistry, it is well known that on finding colouring matters in the products they were examining, chemists usually regarded them as impurities, and the use of animal charcoal and other means were resorted to for the purpose of getting rid of them ; and those who undertook to do the examination of colouring matters themselves were considered as bold men, and not likely to get much result from their labour. Doubtless, there was much truth in this. Hofmann, however, was a bold man, and not one to be daunted, but rather inspired, by difficulties ; and from his results we see how great his success was in this department of chemistry, some of his work proving to be of direct practical value, whilst other parts possessed important bearings both on the practical and scientific development of this subject. His researches on colouring matters extended over a quarter of a century, commencing in 1862 with rosaniline, and ending in 1887 with quinoline red ; and during that period there were but few years in which he did not produce one or more investigations, either related to colouring matters or the products connected with their production.

It will be obvious from what has been said, how Hofmann's early work — after that of Faraday, Unverdorben, Runge,

Fritsche, Mitscherlich, and Zinin—continued to pave the way for the introduction of the coal-tar colour industry, also how the important influence he exercised on the training of his students led in the same direction. I especially refer to Mansfield, who did such valuable work on coal-tar, and Nicholson, whose chemical education under Hofmann was such an important preparation for the work he undertook in after years on rosaniline and its derivatives; and if I may speak for myself, I can only say how much I owe to Hofmann's training, which fitted me to carry out the work which fell to my lot in connection with the introduction and development of this industry. Then if we further consider the importance of the beautiful researches Hofmann made, some of which yielded practical results, throwing fresh light on the nature of the colouring matters and products related to them which were obtained as time went on, some idea may be formed of the contributions made by Hofmann and his school to the coal-tar colour industry.

And yet we must bear in mind that his work in this department of chemistry represents but a small part of all that he accomplished—indeed, the amount of scientific work he did was something marvellous.

X.: 1901

## THE SYNTHESIS OF INDIGO

BY PROFESSOR R. MELDOLA, F.R.S., F.I.C.

(*Journal of the Society of Arts*, 1901, p. 397)

*THIS paper discusses the various synthetical processes which have been used for the production of indigo. The latter portion of the paper is quoted in the article on "The Indigo Crisis": see p. 219.*

XI.: 1901

THE RELATIVE PROGRESS  
OF THE COAL-TAR COLOUR INDUSTRY IN  
ENGLAND AND GERMANY DURING THE  
PAST FIFTEEN YEARS

BY ARTHUR G. GREEN, F.I.C., F.C.S.

(Paper read before the British Association, Section B, Glasgow, 1901)

THE coal-tar colour manufacture has well been called the flower of the chemical industries. Although in absolute money value of its products not equalling some other branches of industrial chemistry, it represents the highest development of applied chemical research and chemical engineering, and may well be taken as the pulse of the whole chemical trade. Indeed, a country which allows the most scientific branch of chemical industry to languish cannot expect to maintain pre-eminence for long in any simpler branch of chemical manufacture; since the skill trained for attacking the difficult problems of organic chemistry is certain sooner or later to be brought to bear on the simpler questions presented in the manufacture of so-called "heavy" chemicals (acids, alkalies, bleach, salts, etc.), and processes hitherto often left to the supervision of foremen will be taken in hand by educated chemists, with consequent improvement in methods of manufacture, better yields, purer products, and cheaper production. The importance of the coal-tar industry cannot therefore be estimated alone by the value of its products, for it exerts a widespread effect upon all other branches of chemical manufacture, from many of which it draws its supplies of raw material. As a pregnant example of this influence, especially noticeable during the last decade, I may mention the revolution which is taking

place in the manufacture of sulphuric acid, that most important product of the "heavy" chemical trade. A strong demand had arisen in the colour industry for a large and cheap supply of sulphuric anhydride, chiefly in connection with the manufacture of alizarin colours and of artificial indigo. With the object of satisfying their own requirements in this respect, the Baden Aniline and Soda Works of Ludwigshafen devoted much time and research to the problem of improving the catalytic process usually known by the name of Winckler, a modification of which process had been worked in this country by Squire Chapman and Messel since 1876. This endeavour was attended with such success that by means of the process and plant which they finally evolved they were enabled to produce sulphuric anhydride so cheaply that not only could it be used as such for a large variety of purposes, but by combination with water afforded a profitable source of sulphuric acid. This new method of manufacturing sulphuric acid is, for concentrated acid at least, cheaper than the chamber process; and since the product is absolutely free from arsenic, and can be produced at any desired concentration, it seems likely to supplant eventually the time-honoured method of manufacture.

Besides exerting this influence upon the inorganic chemical manufactures, the coal-tar industry has given birth during recent years to several important daughter industries. The manufacture of synthetic medicinal agents, artificial perfumes, sweetening materials, antitoxines, nutritives, and photographic developers are all outgrowths of the coal-tar industry, and in great part still remain attached to the colour works where they originated. Of these subsidiary industries the most important is the manufacture of synthetic medicinal preparations, which has already attained to large proportions, and bids fair to revolutionise medical science. The requirements of the coal-tar industry have further led to great advances in the design and production of chemical plant, such as filter-presses, autoclaves, fractionating columns, vacuum pumps and stills, suction filters, enamelled iron, aluminium, and stoneware vessels, etc., for the supply of which extensive works have become necessary.

It is a frequently quoted remark of the late Lord Beaconsfield that the chemical trade of a country is a barometer of its prosperity, and the chemical trade of this country has always been regarded as a most important branch of our manufactures.

Even those who might be inclined to regard our declining position in the colour industry with more or less indifference would consider the loss of a material portion of our general chemical trade as nothing less than a national calamity. As already pointed out, however, the two are indissolubly connected, the coal-tar industry being an essential and inseparable part of the chemical industry as a whole. It is with the object of ascertaining our present and future prospects in the chemical trade of the world that I propose to compare the relative development of the colour industry in England and Germany during the past fifteen years. It was at the commencement of this period, that is to say in the year 1886, that Professor Meldola, in a paper read before the Society of Arts, gave such a masterly account of the position of the industry of this country at that date, and sounded a warning note to our manufacturers and business men regarding its future progress.

If an excuse is required for my venturing to refer again to a subject upon which so much has been said and written already, it is supplied by the fact that the warnings repeatedly given by those who saw the future clearly (notably by Professors Meldola and Armstrong) have remained largely unheeded by our business men. The conclusions which are forced upon us are unfortunately not of a reassuring nature for our national trade, but it is well to remember that nothing is gained by burying our heads in the sand, and that the cure of a disease can only be effected after an accurate diagnosis of its cause.

The period which we have to consider has been one of extraordinary activity and remarkable development in the coal-tar industry, and before I pass to the economic aspect of the question I shall ask you to consider very superficially some of the main points in this advance. In no other industry than this have such extraordinarily rapid changes and gigantic developments taken place in so short a period, developments in which the scientific elucidation of abstract problems has gone hand in hand with inventive capacity, manufacturing skill, and commercial enterprise. In no other industry has the close and intimate interrelation of science and practice been more clearly demonstrated.

Born in 1856, the colour industry had already attained to a considerable state of development by the year 1886. The period prior to this might well be called the "rosaniline period," since it is chiefly marked by the discovery and development of colour-

ing matters of the rosaniline or triphenylmethane group, such as magenta, aniline blue, Hofmann violet, methyl violet, acid magenta, acid violets, phosphine, Victoria blues, auramine, malachite green, and acid greens. Individual members of other groups had already been discovered, but the latter had not yet attained to the importance which they were destined later to occupy. This is especially the case with the class of colouring matters containing the double nitrogen radical known as "azo" colours. This group of compounds has, during the fifteen years which we have to consider, attained to such enormous dimensions and importance that this interval may fairly be termed the "azo period." The number of individual compounds belonging to this class, which have either been prepared or are at present preparable, runs into many millions and far exceeds the members of all other groups of colouring matters put together. In commercial importance also they occupy a position at present far in advance of any other group, the employment of some of them (*e.g.* the "azo" blacks) amounting to many thousands of tons annually. A great stimulus to the investigation of the azo compounds was given by the discovery by Böttiger in 1884 of the first colour possessing a direct affinity for cotton (Congo red), which was followed within a few years by a rapidly increasing series of colours of all shades having similar dyeing properties. The azo colours known prior to this time were either basic colours (aniline yellow, chrysoidine, Bismarck brown, etc.) or acid wool colours (xylidine scarlet, croceine scarlet, etc.). The great simplification of cotton dyeing brought about by the introduction of the new group of azo colours—"benzo" or "diamine" colours as they were called—led to a rapid increase in their number, and compounds containing two, three, four, or more double-nitrogen groups, linking together the residues of various paradiamines (benzidine, tolidine, dianisidine, azoxytoluidine, paraphenylenediamine, naphthylenediamine, etc.) to various naphthol-, amidonaphthol-, and naphthylamine sulphonic acids made their appearance in quick succession. Simultaneously therewith proceeded the discovery and investigation of the various isomeric derivatives of naphthalene required as raw products for the preparation of these colours, an investigation which was largely aided by the classical research on the isomerism of naphthalene compounds carried out in this country by Armstrong and Wynne.



Another method of applying azo colours to cotton, by which much faster shades are obtained, was introduced by Messrs Read Holliday, of Huddersfield, in 1880, and consisted in producing unsulphonated azo compounds on the fibre by direct combination. Owing to the technical difficulties which were at first encountered in applying this process it has only reached its full development during the last few years and at other hands than those of its discoverers. The most important colour produced by this method is paranitraniline red, for which over two hundred tons of chemically pure paranitraniline are manufactured annually.

The search for direct cotton colours led the author in 1887 to the discovery of primuline. This compound, having a direct affinity for cotton and containing at the same time a diazotisable amido group, could be used for the synthesis of various azo colours on the fibre which were remarkable for great fastness to washing. It has had a large employment for the production of fast reds, and the new principle of dyeing which it introduced has been considerably extended in other so-called "diazo" colours. The closer investigation of the thiazol group, to which primuline belongs, further led to the discovery of many other cotton colours belonging to this family, amongst the most important of which are the brilliant greenish-yellow called turmerine or Clayton yellow, the light-fast chlorophenine or chloramine yellow, the pure greenish basic yellow thioflavine, and the fast cotton pink erica.

Passing over the stilbene azo colours and the basic azo ammonium or Janus colours, there remains a class of azo compounds to which I must shortly refer, namely, the mordant azo colours, which with the growing demand for faster shades have recently come into much prominence. In these compounds the presence of an orthohydroxyl or carboxyl group gives to the colour the property (following Liebermann and v. Kostanecki's rule) of combining with metallic mordants, especially chromium oxide, and producing therewith insoluble and fast lakes on the wool or cotton fibre.

We now come to the consideration of three analogously constituted groups of colouring matters, namely, the azines, oxazines, and thiazines. The laborious scientific investigations of Fischer and Hepp, Bernthsen, Kehrman, and others on the constitution of these groups of compounds, the first

members of which (methylene blue, safranine, and Meldola's blue) were discovered in a very early stage of the industry when little or nothing was known of their structure, combined with the theoretical views on the quinonoid structure of such colouring matters promulgated by Armstrong and adopted by Nietzki, led to the discovery of many valuable new members of these classes. Amongst the latter may be specially mentioned the rosindulines, indoine blue, induline scarlet, rhodulines, etc.

Passing to the pyrone and acridine groups in which much investigation has also been conducted, the most notable advances have been the discovery of the rhodamines, a class of pure basic reds, and of the basic yellows and oranges allied to phosphine, namely, acridine yellow, benzoflavine, and acridine orange.

It is in the alizarin group next to the azo group that the greatest progress must be recorded. The demand for fast colours for calico printing and for dyeing chrome-mordanted wool to withstand severe "milling" operations has led to a long series of investigations and patents for producing new derivatives of anthraquinone. These new products, known in commerce as alizarin Bordeaux, alizarin cyanines, anthracene blues, alizarin viridine, alizarin saphirol, etc., are polyoxy- or amido-oxyanthraquinones, for the preparation of which either alizarin or nitroanthraquinones are the usual starting-points.

Passing over some smaller groups, we now come to a very peculiar class of dyestuffs containing sulphur, which although discovered by Croissant and Brettonière in 1873, remained confined to a single representative—Cachou de Laval,—until Raymond Vidal in 1893 obtained a very fast black colouring matter, which dyed unmordanted cotton, by heating para-amidophenol with sulphur and sodium sulphide. The possibility of replacing aniline black in cotton dyeing by a direct colouring matter, and possibly also of obtaining other shades which, though dyed in a single bath, would resist subsequent "cross dyeing" of the wool in mixed fabrics, lent an immense impulse to the study of this class of colouring matters; and although their molecular structure still remains wrapped in obscurity, many new representatives have followed each other in rapid succession ranging in shade from blacks of various hues to browns, olives, greens, and blues. As the most important of these I may

mention Vidal black, immedial black, katigene black, immedial blues, pyrogene blues, katigene brown, katigene green, etc.

It may fairly be claimed, however, that the greatest triumph of the coal-tar industry for the past fifteen years has been the successful production of artificial indigo on a large manufacturing scale.

Returning from the scientific to the economic aspect of the subject, I shall ask you now to consider what share we have obtained in the great expansion of trade resulting from all these new discoveries, many of which have originated in this country. The development of the industry in Germany is well illustrated by the following figures :—

EXPORTS FROM GERMANY TO THE WORLD

	1885.	1895.	1899.
	Tons.	Tons.	Tons.
Aniline oil and salt . . . . .	1713	7,135	—
Coal-tar colours (excl. alizarin). .	4646	15,789	17,639
Alizarin colours . . . . .	4284	8,927	—

Again, if we take values, we find that total exports of coal-tar colours from Germany amounted in 1894 to £2,600,000, and in 1898 to £3,500,000, an increase of nearly a million in four years. The latter figure is practically the same as that given by Perkin as an estimate of the world's total production in 1885, showing how great the increase has been since this date.

The value of Germany's entire production is somewhat difficult to arrive at. Witt, in his report on the German chemical exhibit at the Paris Exhibition, gives as the value of the total chemical industry of Germany for the year 1897 the enormous sum of 46½ million pounds sterling. Of this sum Lefèvre estimates that at least one-tenth may be put down to colouring matters, and another tenth to raw, intermediate, and synthetic products from coal tar other than colours, and he thus assigns for the total annual value of the coal-tar industry of Germany the sum of nine to ten million pounds sterling. With the increase in the production of synthetic indigo, it may be taken to-day to considerably exceed this figure.

One may well wonder what becomes of this enormous quantity of coal-tar products. According to the United States consular reports the  $3\frac{1}{2}$  million pounds' worth of coal-tar colours exported by Germany in 1898 were consumed as follows :—

The United States took	.	.	.	£750,000	worth
The United Kingdom took	.	.	.	730,000	„
Austria and Hungary	„	.	.	350,000	„
Italy	„	.	.	225,000	„
China	„	.	.	270,000	„

whilst the rest of the world took the remainder.

The great increase in production in Germany is further shown by the growth in the capital and number of workpeople employed. Thus according to a report of the Badische Works recently issued, the capital of this company, which was increased in 1889 from £900,000 to £1,050,000, will be further augmented this year by the issue of £750,000 of debentures. The number of workpeople employed by this company in 1900 was 6485, against 4800 in 1896, an increase of over 33 per cent. in four years. The firm of Leopold Cassella & Co., of Mainkur, near Frankfurt, have increased the number of their workpeople from 545 in 1890 to 1800 in 1900.

Passing now to England, we find that the imports of coal-tar colours into the country are steadily rising, as is shown by the following figures taken from the Board of Trade returns :—

IMPORTS OF COAL-TAR DYESTUFFS INTO ENGLAND DURING THE LAST  
FIFTEEN YEARS (EXCLUDING INDIGO)

1886	.	£509,750	1891	.	£586,300	1896	.	£739,300
1887	.	542,000	1892	.	542,200	1897	.	695,400
1888	.	569,000	1893	.	504,000	1898	.	739,000
1889	.	609,200	1894	.	599,000	1899	.	708,800
1890	.	594,400	1895	.	710,000	1900	.	720,000

Contrasted with this, the exports of coal-tar colours manufactured in England have fallen from £530,000 in 1890 to £366,500 in 1899. Comparing these figures with the rapidly increasing export trade of Germany, it is seen that whereas formerly the English export trade in artificial colours was about one-quarter that of Germany, it does not now amount to a tenth part. It is therefore only too apparent that we have had but little share in the great increase which this industry has experi-

enced during the past fifteen years, and that we have not even been able to supply the expansion in our own requirements. In order to ascertain what proportion of our own needs we at present furnish, I am able to lay before you the following interesting figures, which have been kindly supplied to me by the Bradford Dyers' Association and the British Cotton and Wool Dyers' Association, who together form a large proportion of the entire dyeing trade :—

COLOURING MATTERS USED BY BRADFORD DYERS'  
ASSOCIATION

English, 10 per cent. ; German, 80 per cent. ; Swiss, 6 per cent. ; French, 4 per cent.

COLOURING MATTERS USED BY BRITISH COTTON AND WOOL  
DYERS' ASSOCIATION

*Aniline Colours.*—English, 22 per cent. ; foreign, 78 per cent.

*Alizarin Colours.*—English, 1·65 per cent. ; foreign, 98·35 per cent.

The *English Sewing Cotton Company* have also very kindly supplied me with a detailed analysis of their consumption, from which it appears that out of a total of sixty tons of colouring matters and other dyeing materials derived from coal tar only 9 per cent. were of English manufacture.

The following table of statistics of the six largest German firms gives a fair picture of the present dimensions of the industry in that country.

The joint capital of these six firms amounts to at least 2½ millions. They employ together about 500 chemists, 350 engineers and other technologists, 1360 business managers, clerks, travellers, etc., and over 18,000 workpeople. Compared with such figures as these the English colour manufacture assumes insignificant proportions. The total capital invested in the coal-tar colour trade in England probably does not exceed £500,000, the total number of chemists employed cannot be more than thirty or forty, and the number of workmen engaged in the manufacture does not amount to over a thousand.

## POSITION OF THE SIX LARGEST COLOUR WORKS IN GERMANY IN YEAR 1900

—	Badische Aniline Works.	Meister, Lucius & Brüning.	Farbenfabriken Bayer & Co.	Berlin Aniline Co.	Cassella & Co.	Farbwerk Mühlheim, Leonhardt & Co.	Total of six largest firms.
Capital	£1,050,000	£833,000	£882,000	£441,000	Private concern	£157,000	About £2,500,000
Number of chemists	148	120	145	55	} 60	} 450	About 500
Number of engineers, dyers, and other technologists	75	36	175	31			About 350
Commercial staff	305	211	500	150			About 1360
Workpeople	6485	3555	4200	1800	1800		About 18,200
Dividends in 1897	Per cent. 24	Per cent. 26	Per cent. 18	Per cent. 12½	Not known	Per cent. 9	—
Dividends in 1898	„	„	„	15	„	3	—
Dividends in 1899	„	„	„	„	„	5	—
Dividends in 1900	„	20	„	?	„	Nil	—

A similar relative proportion is maintained in the number of patents for new colouring matters and other coal-tar products taken by the English and German firms, as is shown by the following table:—

## COMPARISON OF NUMBER OF COMPLETED ENGLISH PATENTS FOR COAL-TAR PRODUCTS TAKEN DURING 1886-1900 BY SIX LARGEST ENGLISH AND SIX LARGEST GERMAN FIRMS

<i>German Firms</i>		<i>English Firms</i>	
Badische Aniline Works . . .	179	Brooke, Simpson & Spiller . . .	2
Meister, Lucius & Brüning . . .	231	Clayton Aniline Co. . . . .	1
Farbfabriken Bayer & Co. . . .	306	Levinstein . . . . .	2
Berlin Aniline Co. . . . .	119	Read Holliday & Co. . . . .	1
L. Cassella & Co. . . . .	75	Claus & Rée . . . . .	1
Farbwerk Mühlheim, Leonhardt & Co. . . . .	38	W. G. Thompson . . . . .	1
Total of six German firms . . .	948	Total of six English firms . . .	8

Nor does the potential loss which we have sustained by our inability to take advantage of a growing industry represent the

sum total of our losses. The new colouring matters, made almost exclusively in Germany, have in many cases been introduced as substitutes for natural products, which were staple articles of English commerce. Madder and cochineal have been replaced by alizarin and azo scarlets, the employment of many dyewoods has greatly decreased, whilst at the present moment logwood and indigo are seriously threatened. Regarding the indigo question, so much has been written that I do not propose to occupy space in its further discussion, but will only point out that the complete capture of the indigo market by the synthetic product, which would mean a loss to our Indian dependencies of £3,000,000 a year, is regarded by the Badische Company as so absolutely certain that, having already invested nearly a million pounds in the enterprise, they are at present issuing £750,000 of new debenture capital to provide funds to extend their plant for this purpose. In the last annual report of the company they say: "As regards plant indigo, the directors are prepared and determined to meet this competition in all its possible variations in value. Much strange matter has been published in India as to improvements in the cultivation and preparation of natural indigo, but the illusions of the planters and indigo dealers are destined to be dispelled before facts, which, although they are not known to them, will make themselves more felt the larger the production of artificial indigo becomes."

Besides the loss of material wealth which the neglect of the coal-tar trade has involved to the country, there is yet another aspect of the question which is even of more importance than the commercial one. There can be no question that the growth in Germany of a highly scientific industry of large and far-reaching proportions has had an enormous effect in encouraging and stimulating scientific culture and scientific research in *all* branches of knowledge. It has reacted with beneficial effect upon the universities, and has tended to promote scientific thought throughout the land. By its demonstration of the practical importance of purely theoretical conceptions it has had a far-reaching effect on the intellectual life of the nation. How much such a scientific revival is wanted in our country the social and economic history of the past ten years abundantly testifies.

The position with which we are confronted is in truth a lamentable one, and the way out is not so easy to find. In 1886 it could perhaps still be maintained that we held the key to the

situation if we chose to make use of it, inasmuch as the principal raw products of the colour manufacture (tar oils, naphthalene, anthracene, soda, ammonia, iron, etc.) were in great measure imported from England. In a speech to the Academy of Sciences of Munich in 1878 Professor von Baeyer had said: "Germany, which in comparison with England and France possesses such great disadvantages in reference to natural resources, has succeeded by means of her intellectual activity in wresting from both countries a source of national wealth. Germany has no longer to pay any tribute to foreign nations, but is now receiving such tribute from them, and the primary source from which this wealth originates has its home, not in Germany, but in England. It is one of the most singular phenomena in the domain of industrial chemistry that the chief industrial nation and the most practical people in the world has been beaten in the endeavour to turn to profitable account the coal tar which it possesses. We must not, however, rest upon our oars, for we may be sure that England, which at present looks on quietly while we purchase her tar and convert it into colours, selling them to foreign nations at high prices, will unhesitatingly cut off the source of supply as soon as all technical difficulties have been surmounted by the exertions of German manufacturers."<sup>1</sup> Professor von Baeyer could not believe that the English manufacturer and capitalist would stand calmly by and see an important industry which had had its origin and early development in his own country taken from beneath his nose without an effort to retain it. Yet the initial advantages which our natural resources afforded us have been neglected, and now in 1901 the conditions are completely changed. The adaptation of condensing plant to the Westphalian coke ovens has rendered Germany, though still a large buyer from England, no longer dependent on English tar and ammonia; by the development of the ammonia-soda process she no longer requires English alkali; whilst all other raw products of the colour industry can now be purchased in the commercial centres of Germany at least as cheaply as in England, and some even at lower prices. Through the shortsightedness, ignorance, and want of enterprise of those with whom the care of the colour industry in this country has rested, the opportunity has been allowed to pass for ever. The English capitalist has passed over as not sufficiently profitable for his consideration an industry

<sup>1</sup> Quoted by Mr Levinstein, *Jour. Soc. Chem. Ind.*, 1886, p. 350.



which at present amounts to nine or ten million sterling annually, and from which his German confrère reaps a dividend of nearly 20 per cent. The English manufacturer has considered that a knowledge of the benzol market was of greater importance than a knowledge of the benzol theory, and after the early but brilliant days in the infancy of the industry, when guided by such eminent workers as Hofmann, Perkin, and Nicholson, commercial progress and scientific investigation went hand in hand, but little encouragement has been given here to chemical investigators and discoverers. The control of the industry unfortunately soon passed into the hands of men who had no knowledge and absolutely no appreciation of the science upon which their business rested, and, concerned only with getting the ultimate amount of present profit, discouraged all scientific investigations as waste of time and money. The chemist who devoted himself to the elucidation of the chemical constitution of a colouring matter was regarded by them as an unpractical theorist of no value to a manufacturing business. Even when he discovered new colouring matters of commercial value they were so blind to their own interests, and so incapable of believing that any practical good could come out of such theoretical work, that in many cases they refused to patent or in any way take advantage of the discoveries made by him. During recent years this attitude has certainly undergone considerable modification, and some attempt has been made to call in the aid of the science so long neglected. Certain firms, indeed, must be given the credit of endeavouring to pursue a more enlightened policy, but these attempts have been of a more or less sporadic nature and always directed too much in the expectation of realising immediate financial results. The difficulties which must be encountered in the attempt to regain the lost ground are of necessity very great, and are quite unappreciated by our business men. It seems, in fact, to have been the opinion of the public and the average financial man that this industry ought to be easily won back by us by the establishment of a few technical schools, the engagement of a dozen chemists, and the investment of a few thousand pounds in new plant, forgetting that the supremacy of our German competitors has been gained by years of patient toil, by the work of hundreds of trained chemists, and by the outlay of millions of capital. Who can be surprised therefore if such expectations have not been realised, and if in spite of some notable successes the general

position of the colour trade in England at the present day, at a time when even the German trade is suffering from the general depression, looks worse than at any previous period? During years of stagnation in this country the German manufacturers have been realising large profits, which they have employed in consolidating their businesses, writing off the value of their buildings and plant, and accumulating enormous reserves (the reserve of the Badische Company is over a million pounds): they have gathered round them perfectly working organisations, comprising enormous staffs of scientifically and practically trained research chemists, factory chemists with highly specialised knowledge, chemical engineers, dyers, and others; their travellers and agents are in every part of the globe; by long manufacturing experience and unremitting endeavour to improve their processes and plant they have brought the yields and quality of their products to such a state of perfection that even when the manufacture of these products is no longer covered by patents they are able to produce them at a cost price which is impossible to anyone commencing their manufacture; they have hedged themselves about with a perfect stockade of many hundreds of patents, have accumulated in their laboratories thousands of intermediate products ready at any time to be subjected to any new treatment or combination which research or theory may suggest as likely to yield new results. By the complete range of colours which they are able to offer in each group of dyestuffs, whether basic colours, acid colours for wool, fast colours dyeing on metallic mordants, diazotisable colours, or direct colours for cotton, and by the invaluable aid and assistance which they can give the dyer in his daily work they are enabled to retain his custom even if it sometimes happens that a better and a cheaper article is offered him by the home producer.

Where, then, are we to look for an improvement? Some would find a remedy in the imposition of heavy protective tariffs; but such tariffs in France have not availed to prevent a similar state of things there, and protection in colouring matters might have a very detrimental effect upon the textile industries of the country. Others expect salvation from the extension of technical schools; but, laudable as is the aim of these institutions, I cannot see how they can effect much until their raw material is of a very different character from what it is at present, and until the public can be completely disabused of the fallacy that a year or two of

technical training pumped into an ignorant schoolboy will produce a better works chemist than a university course of scientific study laid upon the foundation of a good general education. Mr Levinstein again bases his hopes for the future upon a reform of the patent laws, and seeks to compel all patented processes to be worked in this country. Although I am inclined to believe that a portion of our present troubles has been brought about by bad patent law, framed mainly from an engineering and not from a chemical point of view, which seems specially designed to foster foreign trade at our own expense, yet I cannot attribute to this cause a too preponderating influence, and am doubtful whether its removal now would materially improve the position. The remedy for the present state of affairs must of necessity be a slow one, and in my opinion can only be found in a better appreciation of the value of science throughout the length and breadth of the land. Until our Government and public men can be brought to realise the importance of fostering the study of science and of encouraging all scientific industries, until our schools and universities appreciate the importance of a scientific education, until the rewards for public services in science are made equal to those in other branches of the public service, so long will science continue to be held in insufficient esteem in our country, and the best and most promising of our rising young men will be deterred from adopting chemistry as a profession. It is not so much the education of our chemists which is at fault as the scientific education of the public as a whole.

XII.: 1901

## THE INDIGO CRISIS

(*Journal of the Society of Dyers and Colourists*, 1901, p. 157)

It is now generally recognised that the threatened replacement of natural indigo by the synthetic product is a matter not only of scientific interest, but one which may have far-reaching economic and political consequences ; and mainly on this account the public interest has been aroused to an extent which is very unusual in matters of this character. This has been reflected by questions in Parliament and correspondence in the *Times*, *Nature*, and other papers, as well as in the more directly concerned trade journals.

Another reason for the widespread interest evinced is the very impressive manner in which the problem of the artificial production of indigotin has been attacked. The fact that about £1,000,000 has been spent by a single German firm in working out the process and in preparing for the commercial introduction of the product has appealed to the public imagination as a concrete example of German enterprise, and has also led many to realise the magnitude of the interests involved.

Within the last few years many papers and notes on natural and artificial indigo have appeared in this Journal, and the various aspects of the subject will be more or less familiar to members, but the general interest was greatly intensified by the publication of the lectures delivered by Professor von Baeyer and Dr Brunck at the opening of the Hofmann House in Berlin in October 1900. Von Baeyer's lecture dealt chiefly with the theoretical aspect of the question, while Dr Brunck dealt mainly with the manufacturing and commercial side.

Dr Brunck's lecture will undoubtedly become historical, and a translation is given almost *in extenso* :—

THE HISTORY OF THE DEVELOPMENT OF THE  
MANUFACTURE OF INDIGO

In 1868 the first complete synthesis of a vegetable colouring matter was accomplished. Graebe and Liebermann had pointed out the path from anthracene to alizarin, and chemical industry hastened to follow that path. Magnificent was the result of this undertaking, and the industry of coal-tar colours gained a victory which justified its further hopes and gave it the courage to direct its efforts toward a still higher goal, namely, the conquest of the oldest and most important of all colouring matters, indigo.

The observation by Emmerling and Engler, that indigo could be made from orthonitroacetophenone, did not supply chemical industry with an effective base. However, after Ad. Baeyer had added the synthesis of isatin to his previous synthesis of indigo from the former, he discovered, in 1880, his beautiful synthesis of indigo from orthonitrophenylpropionic acid, and thus, from an industrial point of view, the question of manufacturing indigo synthetically assumed concrete and definite form.

Orthonitrophenylpropionic acid is a derivative of cinnamic acid; the latter could, at that time, be made by means of "Perkin's reaction" from benzaldehyde, and this, since the introduction of malachite green into the arts, had become a product much employed in the coal-tar colour industry, and was easily made from toluene.

The Badische Anilin- und Soda-Fabrik and the Farbwerke vorm. Meister, Lucius & Brüning, at Höchst-on-the-Main, acquired Baeyer's patents, and now, in conjunction with the inventor, they began the technical investigation of the problem, which was destined to occupy a period of more than twenty years.

The task was begun with enthusiasm, and the phases of the individual syntheses were systematically investigated and studied. Of the circumspection and thoroughness with which the subject was studied in all its aspects, but slight conception is given by the patents subsequently taken out.

I have before me a tabulation of all the patents bearing on this subject, and it shows that in Germany alone there are 152 patented inventions.

It soon became possible to replace "Perkin's process" of making cinnamic acid by the benzal chloride and sodium acetate process. Through this process, cinnamic acid became a cheap article of manufacture, instead of being an expensive laboratory preparation. But, on the other hand, orthonitrocinnamic acid was at first, comparatively, very expensive.

On nitrating cinnamic acid according to the methods then in use, only a small portion of the cinnamic acid was converted into the orthonitro compound, while the greater part was converted into the paranitro derivative, which is not available for the production of indigo.

It was, therefore, necessary to alter this unfavourable result, and by employing cinnamic acid ester in place of the free acid, it was possible to so conduct the operation that 70 per cent. of the acid could be converted into the orthonitro compound.

The subsequent bromination of the orthonitrocinnamic acid, as well as the conversion of the resulting dibromide of this acid into orthonitrophenylpropionic acid, still offered many difficulties. But the investigations were carried on with enthusiasm and with energy, and, as early as the spring of 1881, they had so far progressed that it was possible to continuously manufacture the "propionic acid."

This process, however, was not available for the direct manufacture of indigo, because of the high cost of production, which, in spite of ease of execution and of good yields, exceeded that of the vegetable product.

However, attempts were made in other directions to render "propionic acid" of use in the arts.

At that time indigo printing was a secret of but few firms, and was an operation requiring much experience. This circumstance suggested the conversion of "propionic acid" into indigo upon the fibre, and this conversion was possible after Caro had discovered in sodium xanthate a reducing agent suitable for this purpose.

"Propionic acid" was introduced into cotton printing, and was employed especially for the production of those delicate patterns which had hitherto been produced by means of indigo, according to the then prevailing methods, but only with difficulty. Unfortunately, however, this success was more of a theoretical than of a practical nature, for "propionic acid" was never used generally.

Although the results of this painstaking labour did not fulfil the expectations of the workers, this fact did not shake their confidence nor diminish their activity. They recognised in the results and the experience so far collected, a foundation upon which it was possible to base further work.

The year 1882 brought with it Baeyer and Drewsen's synthesis of indigo from orthonitrobenzaldehyde and acetone. This process, which likewise passed into the possession of the Farbwerke, at Hoechst, and of the Badische, was, in turn, subjected to technical investigation. The formation of indigo was, indeed, more smooth than by means of the cinnamic acid process, but the development of a rational method of manufacture of orthonitrobenzaldehyde was beset with difficulties which at first appeared insurmountable.

After it had been determined that, in spite of the greatest possible variations of the conditions observed, the direct nitration of benzaldehyde yielded only insufficient amounts of the orthonitro derivative, which was accompanied by metanitrobenzaldehyde, which is useless for indigo manufacture, orthonitrobenzyl chloride was employed as the initial material for the production of orthonitrobenzaldehyde; this orthonitrobenzyl chloride is formed along with the paranitro body by the nitration of benzyl chloride, but again, only in subordinate quantities. All attempts to arrive at a better result failed.

There now remained the possibility of converting orthonitrotoluene into orthonitrobenzaldehyde, either by chlorination and subsequent oxidation, or by direct oxidation. These experiments were carried on for years, but the difficulties in the way of completely chlorinating orthonitrotoluene, and satisfactorily working up the chlorination product could not, for the time being, be overcome.

When, in 1886, the Badische Anilin- und Soda-Fabrik had found the method, which has recently also been patented by the Société des Usines du Rhône ancien. Gilliard, Monnet and Cartier, of directly oxidising methyl derivatives of benzene to the corresponding aldehydes, without intermediate conversion into chlorination products, hope was again entertained of arriving at orthonitrobenzaldehyde by oxidising orthonitrotoluene. However, these experiments were unsatisfactory and appeared to be without a practical future. The probability that orthonitrobenzaldehyde would serve as a starting-point for the synthetic

production of indigo became more and more remote. The cost of production of synthetic indigo was not only dependent upon the price of toluene, which was available in but limited quantity, but also upon the utilisation of the paranitro by-product.

In 1893 the synthesis of indigo from orthonitrobenzaldehyde was made technically available by Kalle & Co., in a manner similar to the way in which the "propiolic acid" process had already been applied. This firm succeeded in converting the intermediate product arising during the formation of indigo from the aldehyde and acetone, namely, orthonitrophenyllactone, into a soluble bisulphite compound, and this found application in printing. This product, which Kalle & Co. have placed upon the market as "indigo salt," is employed for the purposes of printing indigo upon cotton, and is superior to "propiolic acid," on account of the ease of its application.

It almost seemed as though the investigation of this branch of the subject had ceased. Several years passed by, during which not a single new observation or fact connected therewith was published. It was not until 1896, and when, indeed, it seemed extremely likely that we should solve the problem of a technical indigo synthesis along lines which we had followed in the meantime, that it appeared from published patents that this apparently abandoned field had, nevertheless, been assiduously cultivated. The Farbwerke, at Hoechst, had arrived at a technically useful process of converting orthonitrotoluene into orthonitrobenzaldehyde by treating the mixture of products obtained on chlorinating orthonitrotoluene with aniline or aniline sulphonic acid, and which can then be readily isolated. The product so obtained is converted into the corresponding benzylidene compound, which latter, on treatment with acids, is converted into orthonitrobenzaldehyde, and aniline or aniline sulphonic acid.

The method of producing orthonitrobenzaldehyde by direct oxidation of orthonitrotoluene to its aldehyde has since been further developed by the Société des Usines du Rhône, as well as by us, the Badische Anilin- und Soda-Fabrik, and now yields better results.

While it is thus possible to produce orthonitrobenzaldehyde, the conditions for the manufacture of indigo from this substance are, at present, so far favourable, that, on account of the increased consumption of paranitrotoluene during the last few years, there has arisen a corresponding surplus of orthonitrotoluene as a by-



product. But the amount of indigo which could be manufactured therefrom would necessarily be confined to narrow limits, and could constitute but a small part of the consumption.

If, however, this branch of chemical industry were so situated as to be able to entirely disregard the utilisation of the paranitro by-product, yet its ability to expand and to increase would always be circumscribed, and its foundation would be uncertain, so long as its initial material, toluene, is available in but limited quantity.

Permit me, in explanation of the foregoing, to call your attention to some statistical figures. Benzene and toluene are principally used in the manufacture of coal-tar colours, and their intermediate products, and their annual production is at present about 25,000 to 30,000 tons. On an average, there will be produced about four parts of benzene for every one part of toluene. Consequently, there are annually available about 5000 or 6000 tons of toluene, which are just about sufficient to satisfy the present needs. The market value of toluene is, as against previous years, considerably higher than that of benzene, and with increasing demand for toluene, its market value must rise, so long as the amount of available toluene, which is regulated by the demand for benzene, does not increase.

The toluene now on the market not being available for the manufacture of indigo, it would be necessary to obtain a new supply of toluene.

This would mean that for every ton of toluene thus obtained, four tons of benzene would have to be made; some use would, therefore, have to be found for this benzene.

According to a recent published statement concerning the yield of indigo from toluene, by the newest and best technical methods, one pound of indigo requires about four pounds of toluene. Therefore, the total amount of toluene now produced would suffice, at most, for the production of one-quarter of the world's consumption of indigo, which may be estimated at about 11,000,000 pounds of 100 per cent. strength; that is, it would be necessary to add to the present production of coal-tar hydrocarbons four times the amount which is made at present, in order to completely replace vegetable indigo.

On account of this state of affairs, we have for a long time had but little hope that the indigo syntheses which I have so far discussed could ever be capable of producing indigo in large

quantity, *i.e.* completely replacing vegetable indigo. It was, therefore, necessary for us to direct our efforts towards obtaining an indigo synthesis which was based upon an easily accessible initial material, and, above all, an initial material whose supply was sufficient and adequate.

It was then—that is, in 1890—that the chemical world was astounded by the discovery of Heumann, namely, that indigo could be obtained by melting phenylglycocoll with caustic potash.

Through this discovery, the question of the technical production of indigo was placed upon a new basis; the efforts of the industry in this direction were, by this means, led into new and promising paths. Promising, because this new synthesis fulfilled the first requirement of manufacture on a large scale, namely, the cheap and easy production of the required initial materials which, in this case, were solely aniline, acetic acid, chlorine, and alkali.

This invention was likewise acquired by the Badische Anilin- und Soda-Fabrik, and the Farbwerke at Hoechst, who at once took up the technical investigation of this subject, at first with the assistance of the inventor, but he, unfortunately, died in 1894, and so did not see the completion of the structure founded upon his last researches.

Although the Heumann synthesis fulfilled the first requirement for technical availability, namely, the easy supply of the initial materials, nevertheless it did not satisfy the requirements with respect to the yield of dyestuff. Although, after numberless experiments, it was possible to improve this yield, yet the improvement was not such as to make manufacture profitable.

Experiments to obtain a more satisfactory formation of indigo by substituting for the alkali-melt another condensation agent, led us, and later also the Farbenfabriken vorm. Friedr. Bayer & Co., at Elberfeld, to the observation that an indigo-sulpho acid could be obtained from phenylglycocoll by the action of fuming sulphuric acid. However, this sulpho acid does not possess the good dyeing properties which are possessed by the sulpho acid obtained by the sulphonation of indigo, and this process likewise remained without technical application.

The hopes which had been placed in phenylglycocoll as the basis for an indigo synthesis proved vain.

Other glycocolls behaved similarly to phenylglycocoll. Toly-, xylylglycoll, and the glycocolls of the naphthylamines yielded

scarcely any colouring matter, or such small amounts that it was impossible for them to come into consideration at all. Further, it had been ascertained that the derivatives of indigo were inferior to indigo itself, so far as beauty of shade is concerned, and did not meet the demands of the dyer.

But Heumann had also found that the glycocoll of anthranilic acid, that is, phenylglycocoll-orthocarboxylic acid, likewise yields indigo when treated in a similar manner. In this case the formation of indigo takes place far more smoothly, and experiments soon made it appear that this process was capable of development and perfection. But the industrial realisation of this synthesis, for which the production of anthranilic acid as initial material was needed, involved conditions far less favourable than those for the production of phenylglycocoll, and was beset by extraordinary difficulties, which at times appeared insurmountable. These could be cleared away only by men who, in addition to possessing a thorough and a broad chemical knowledge, likewise possessed great technical skill, and who were experienced in solving difficult chemical problems, organic as well as inorganic, attacking them with persistence and with ingenuity, and finally bringing them to a successful issue. Fortunately, we had the assistance of such men, and after almost seven years of labour we succeeded in solving the problem.

This now brings me to a discussion of the development of the process of manufacturing indigo as it is to-day carried on by us. Phenylglycocoll-orthocarboxylic acid is produced from anthranilic acid and monochloroacetic acid. For the manufacture of the former we were at first dependent upon orthonitrotoluene; orthonitrotoluene could be oxidised to nitrobenzoic acid, and this could then be reduced, or the operations could be reversed, and the reduction product of orthonitrotoluene, namely, orthotoluidine, could be oxidised in appropriate manner (*e.g.* by means of its acetyl compound) to anthranilic acid. This process, however, was beset by the same obstacles as was the manufacture of indigo from orthonitrobenzaldehyde. But this was not to prove fatal, for there was a process available, which had been discovered in 1890 by Hoogewerff and Van Dorp, and which, starting from phthalic acid, produced anthranilic acid. It was A. W. von Hofmann who, by his gifted investigation of the peculiar action of alkaline solutions of bromine upon amines, furnished these investigators with the basis for their researches. They succeeded

in converting phthalimide into anthranilic acid by means of an alkaline solution of bromine.

With phthalic acid as initial material for anthranilic acid, naphthalene became the initial material of the indigo synthesis, and this fact created the first reliable basis for indigo manufacture on a large scale.

From this time on I was firmly convinced that the path which was now being followed must lead to the achievement of the great object: The replacement of vegetable indigo by synthetic indigo.

In fact, naphthalene is an initial material which, for the purpose of indigo manufacture, is available in unlimited quantities. Based upon reliable information, I estimate that the amount of coal tar which is annually treated for its contained hydrocarbons, and which I assume to be two-thirds of the total world's output, contains from 40,000 to 50,000 tons of naphthalene, and of this only about 15,000 tons, which correspond to the present-day consumption, are isolated. For the purposes of indigo manufacture, therefore, there remain at least 25,000 tons of naphthalene which hitherto, on account of lack of market, were burned to lamp-black or remained dissolved in the heavy oils, but which can also be isolated by the same means and at the same cost as the aforementioned 15,000 tons.

The naphthalene in this way available is, however, more than sufficient to cover the amount required for the manufacture of the world's consumption of indigo.

The auspices for the solution of this great problem were therefore favourable, and it became necessary to bring to bear upon its accomplishment all the ability and energy and all the expedients and means known to the present-day industry, and to make use of all the experience which had been acquired in manufacturing operations in the course of a great number of years, and to spare no labour and no expense in order to make everything, which could possibly contribute to its success, serviceable to this undertaking.

And, in fact, there was a great work still to be performed. The systematic investigation of the individual phases of the process occupied the attention and activity of our best men through many years.

We did, indeed, at that time possess the best process then known for the manufacture of phthalic acid. This consisted in

the oxidation of naphthalene by means of chromic acid, and it had been first developed and perfected by us, and had been in operation for twenty years. But, since phthalic acid so produced was still too expensive, and it was not to be expected that this method of manufacture which had been employed by us for so long a time was still susceptible of an essential improvement, it was necessary to bring about the oxidation of naphthalene by a cheaper means.

Our chemist, E. Sapper, succeeded in finding an entirely new method for the production of phthalic acid, which consisted in heating naphthalene with highly concentrated sulphuric acid.

A most comprehensive series of experiments was carried out to develop this process to practical utility. The effect of additions of the most various kinds to the reaction mass was tried, and, in the end, mercury was found to be an agent which brought the yields to a satisfactory point. Even though an accident, namely, the destruction of a pocket containing mercury, was an assistance, this accident merely hastened the solution of the problem. But without it the object would certainly have been achieved.

On a small scale, the results were perfect. But the manufacture on a large scale required enormous efforts, much time and patience, and the question of apparatus especially required many and very expensive experiments for its solution.

In the first place, the oxidation of the naphthalene required large amounts of strong sulphuric acid, and the nearly complete and most advantageous recovery of this was the prime condition of success. Had we been compelled to accomplish this regeneration of the sulphuric acid in lead chambers, then this new process would hardly have offered any advantages over the chromic-acid process.

It was at this stage that our new sulphuric-acid process, which was developed by R. Knietzsch, stood us in good stead. The contact process, which had become available for the industrial production of fuming sulphuric acid, through the suggestion of C. Winkler, in 1875, has since been developed by us so that the production of sulphuric anhydride, by the direct union of pyrites burner gases—that is, of sulphur dioxide and the oxygen of the air,—has now become more profitable for the manufacture of sulphuric acid than is the lead-chamber process. This has been published both in chemical literature and in our patents.

Our new process of making phthalic acid was, therefore, directly dependent upon this sulphuric acid manufacture, since the latter made it possible to directly convert the sulphur dioxide arising from the oxidation of the naphthalene into concentrated sulphuric acid in the cheapest possible manner.

You may be able to form an idea as to the part which this sulphuric-acid manufacture plays in our process from the fact that, from our present production of phthalic acid, there result annually 35,000 to 40,000 tons sulphur dioxide which we must reconvert into sulphuric anhydride. For this purpose a plant of about the same size is required as for an equal weight of iron pyrites.

Now, and only now, was the cycle of the process completed. The oxygen of the air now converts naphthalene into phthalic acid in the cheapest manner possible, and our new sulphuric-acid process thus becomes one of the foundations of indigo manufacture. This is a firm foundation !

While these labours, which extended from 1891 until 1897, were in progress, the manufacture of the other initial materials was investigated and worked out with the same energy.

Large amounts of chlorine are required in the manufacture of the requisite amount of chloracetic acid, and also for the oxidation of phthalimide to anthranilic acid, and it was therefore necessary to create a cheap source of chlorine. Even now we must chlorinate 4,400,000 lb. of glacial acetic acid—an amount of acetic acid equivalent to 130,000 cubic yards of wood ! Neither Weldon's process nor Deacon's process would answer our purpose ; the former, because the chlorine it yielded was too expensive, and the latter, because its chlorine was too dilute.

In the meantime, however, the researches on the electrolytic production of chlorine from alkali chlorides had made considerable strides. A number of electrolytic processes were, indeed, known by name, but their real value was not known, and it was therefore necessary to select from these that process which was best adapted to the requirements of indigo manufacture ; and, since great expenditure is involved in plant of this nature, it was necessary to exercise the greatest caution in this selection.

We believe that we are justified in holding that, through acquiring the process of the Chemische Fabrik Elektron in Griesheim-on-the-Main, we possess the best process of the present day.

Only in point of purity the resulting chlorine did not satisfy our high requirements, and here our process for the liquefaction of chlorine enabled us to convert it into its purest form. The development of the process for the production of chloracetic acid was also a difficult task ; however, this branch of manufacture, which, at first, was most disagreeable, has finally developed into a comparatively simple manufacturing operation.

The manufacture of phthalimide, of anthranilic acid, and of phenylglycocoll-orthocarboxylic acid itself, the real mother-substance of indigo, was more difficult than it at first appeared to be. Whole series of systematic experiments had to be carried out, in order to determine the conditions under which it was possible to obtain a maximum yield of pure acid.

One of the most difficult problems was the proper carrying out of the melting process on the large scale ; that is, the conversion of phenylglycocoll-orthocarboxylic acid, by heating it with alkali, into the leuco compound which, on oxidation with air, yields indigo. These experiments, in the execution of which R. Knietzsch, the able and successful manager of our indigo department, and P. Seidel took most active part, were carried on for years. New apparatus had to be invented and constructed before the process was so far developed as to be adapted for continuous manufacture.

It may be mentioned, in passing, that during the determination of those conditions which would bring about a satisfactory course of the melting operation, free indoxylic acid was manufactured which, under the name "indophor," has found application in cotton printing, namely, for the production of indigo upon the fibre in a manner similar to that in which "propionic acid" and "indigo salt" are employed.

The indigo which is obtained from the water solution of this melt, by means of air, is crystalline. In those cases where an especially fine state of division is desired, such as in the fermentation vat, the so-obtained indigo is converted into a sulphate by means of sulphuric acid, and this is decomposed with water, and is thus reconverted into the original indigo in the form of a loose powder, which is extremely easily soluble in the vat.

I have attempted to present to you, in a short sketch, the history of the development of a new manufacture, and it now devolves upon me to more clearly bring out a few considerations which may be adapted to indicate, at least, the influence of this

manufacture upon the development of important industries, as well as upon future economic changes.

The advantages which the synthetic product possesses over the vegetable product have been presented so frequently on other occasions, that in this direction I can be very brief.

The uniformity and the constant strength of synthetic indigo, its absolute freedom from foreign admixture, its easy reducibility when finely divided, and the ease of application which is thereby secured for the dyer, are to be mentioned as its principal advantages, as against the constantly varying strength and the difficult reducibility of the commercial brands of vegetable indigo. These advantages free the dyer from oppressive dependence upon the dealers, because, on account of lack of methods of accurate determination, he has been obliged to purchase his stock, not according to its actual value, but according to external and easily misleading characteristics. These advantages of the synthetic product now guarantee him absolute uniformity and perfect quality.

In spite of these advantages, synthetic indigo had to overcome many obstacles which were placed in the way of its introduction. It was but natural that its quality was discredited by those to whose interest it was to do so; this was done, for example, by stating that the impurities contained in vegetable indigo, and which were absent from the synthetic product, were essential to the dyeing process. Again, it was claimed that the indigo which we brought into commerce was nothing more nor less than refined vegetable indigo!

One of the greatest obstacles in the way of its introduction, however, was the fact that the conception of a "chemical individual" is for the most part unknown to those who are not chemists. It was impossible for such to comprehend the fact that two bodies of different origin, such as vegetable indigo and synthetic indigo, could be identical; synthetic indigo was designated as a substitute and adulterant of vegetable indigo, and it was attempted to place it on the same plane with those aniline dyestuffs that dye a similar shade.

But such deceptions and carpings could not long prevail against the facts.

Synthetic indigo, in accordance with its very great purity, yields brighter shades. Curiously enough, this circumstance also acted at first, though of course only in isolated instances, as an



obstacle to its introduction ; thus, for example, one or two of the German military authorities raised an objection because cloth dyed with our pure indigo possessed a somewhat brighter shade than did cloth which had been dyed according to the old method, with impure indigo, and which served as the standard of comparison.

On account of its easy reducibility and uniformity, dyeing with pure indigo has become an operation equal in ease and simplicity with the dyeing with any other ordinary dyestuff, whilst, formerly, it was only possible after acquiring considerable experience by prolonged practice to obtain a desired shade with certainty, when using vegetable indigo, which, as is known, is available only in brands of the most varying degrees of purity. This latter art, which is often inherited from generation to generation, has lost much of its value through synthetic indigo, and on this account the new product was accorded a most unfriendly reception by many an indigo dyer who was conscious of his own especial skill.

When, in July 1897, we had succeeded in so far reducing the cost of manufacture of synthetic indigo that we could successfully compete with the lowest price which vegetable indigo had ever reached, we decided to first erect a plant which would enable us to supply the consumption of this colouring matter in Germany, and in so doing arrangements were made so that, in case of success, our capacity could be increased at will.

As we were ignorant as to how cheaply the planters could supply vegetable indigo in the course of the impending conflict, and also because there is a possibility that a cheaper and simpler process for the manufacture of indigo might be found, our venture was subject to a very great risk ; because, for its successful prosecution, extraordinary financial resources were necessary, and, as a matter of fact, we have, to-day, invested about £900,000 for this purpose.

Up to the present, the results which we have achieved correspond to our expectations, and we hope to be victorious in the long and arduous struggle that is before us.

Formerly, the value of the indigo annually produced was estimated at £4,000,000 to £5,000,000 ; even at the present prices, which are essentially lower, the value may still be £2,500,000 to £3,000,000.

Although, up to the present, we have succeeded in securing

to German industry but a part of this sum, and thereby making the German consumer independent of foreign countries, and in retaining for Germany those sums of money which have hitherto been paid to foreigners for indigo, yet it is probably merely a question of time when the entire consumption of indigo will be provided for synthetically, and thus large sums will pass from foreign countries to Germany.

The quantity of indigo which we produce annually, even at this date, would require the cultivation of an area of more than a quarter of a million acres of land (390 square miles) in the home of the indigo plant. The first impression which this fact may be likely to produce is that the manufacture of indigo will cause a terrible calamity to arise in that country; but perhaps not. If one recalls to mind that India is periodically afflicted with famine, one ought not, without further consideration, to cast aside the hope that it might be good fortune for that country if the immense areas, now devoted to a crop which is subject to many vicissitudes and to violent market changes, were at last to be given over to the raising of breadstuffs and other food-products. For myself, I do not assume to be an impartial adviser in this matter, but, nevertheless, I venture to express my conviction that the Government of India will be rendering a very great service if it should support and aid the progress, which will in any case be irresistible, of this impending change in the cultivation of that country, and would support and direct its methodical and rational execution.

I have reached the end of my lecture. You have seen that this new industry is not an unexpected gift fallen from the heavens, but that in order to complete the task the intellectual labour and the industry of many men had to be co-ordinated, in an organised attempt to attain a definite object, for a number of years, and throughout a considerable period when success could by no means be regarded as certain. The pre-requisites for practical indigo synthesis were supplied by the results of long years of scientific labour. All the expedients of an advanced art were at command, and it is to the wide knowledge, to the industry, to the energy, and to the faithfulness to duty which characterise our German chemists that the final completion of the work is due, a work of which we wish that it may signify an advance in civilisation, and which we hope will be an honour to the German chemical industry and a blessing to our country.

## OTHER OPINIONS

In a recent lecture before the Society of Arts,<sup>1</sup> Professor Meldola discussed the various synthetical processes for the manufacture of indigo, and more especially the manufacture of "indigo pure" by the Badische Aniline Co.

With regard to the all-important point of cost of production, Professor Meldola offers the following remarks :—"Naphthalene is the hydrocarbon which exists in coal tar to a larger extent than any other. The average quantity is about 8 per cent., and there is any amount of it to be had. The whole of the naphthalene in tar is not at present extracted, the chief supply being furnished by the middle or carbolic acid fraction. Mr T. Wilton, of the Gaslight and Coke Co., states that that company produces about  $19\frac{1}{2}$  million gallons of tar annually. This company alone would thus be able to supply over 15 million pounds of naphthalene per annum. The purified hydrocarbon has a present market value of £18, 10s. per ton, which is less than one penny per pound. From an estimate supplied by Mr Charles Tyrer, of Thomas Tyrer & Co., it appears that technical chloracetic acid might probably be made at about 1s. 1d. per pound. As regards the supply of naphthalene, it has been suggested that the production from coal tar would be insufficient to meet the demand, supposing that all the indigo now required were made synthetically." Figures given by Dr Brunck refute this statement. (See page 212.)

It may be added also that coal tar is not the only source of naphthalene, since a considerable quantity of this hydrocarbon is contained in coke-oven tar. Moreover, petroleum may be looked upon as a potential source of naphthalene, since the crude naphtha, consisting chiefly of heptane and octane, on decomposition by heat, gives a mixture of hydrocarbons containing, according to Worstall and Burwell,<sup>2</sup> 12.5 parts benzene, 3 parts toluene, 3 parts xylene, and 3.6 parts naphthalene for 100 parts naphtha.

With respect to the probabilities of the issue of the conflict between natural and synthetic indigo, Professor Meldola, while not regarding the cause of the indigo planters as a forlorn one,

<sup>1</sup> *Jour. Soc. Arts*, 19th April 1901.

<sup>2</sup> *Amer. Chem. Jour.*, 1897, x. 815.

considers the outlook as gloomy, in view of the probability of the Badische process being still further perfected and cheapened.<sup>1</sup>

The magnitude of the operations of the large German colour works has often been the subject of remark in these columns, but their remarkable growth and the unbounded enterprise with which they are conducted is very succinctly put in the following paragraph from Professor Meldola's lecture :—

“The factory at Ludwigshafen employs 148 scientific chemists, 75 engineers and technical experts, and 303 members of the mercantile staff. In 1865 they commenced with 30 workmen, and they now employ 6000. The consumption of coal is about 243,000 tons per annum. Water is supplied to the factory to the extent of 20,000,000 cubic metres (4,400,000,000 gallons) annually ; they make 12,000,000 kilograms (11,400 tons) of ice, and 12,000,000 cubic metres (420,000,000 cubic feet) of coal gas in the course of a year. 102 boilers supply steam, which serves for heating purposes and for driving 253 steam engines. The factory comprises an area of 206 hectares (510 acres), of which 317,429 square metres (378,000 square yards) are built upon.”

In October of last year a Commission was appointed by the Government of India to inquire into the condition of the sugar and indigo industries, and their report, which has already been issued, is reviewed in the *Times* of 15th April 1901. It is there stated that the average acreage in India under indigo during the five years 1893–98 was 1,406,000 acres, but in 1899 it was only 1,027,000 acres, and in 1900, 964,000 acres. In 1895–96 the exports amounted to 187,000 cwts., but steadily declined to 111,000 cwts. in 1899–1900. This was partly due to unfavourable seasons ; but in the past experience of the trade, a low output was always accompanied by an enhanced price ; whereas, in the period referred to, the price in the poor years did not show the same recovery, and the Commissioners conclude that it is reasonable to anticipate that the competition of synthetic indigo will prevent any future increase in the price of vegetable indigo, and that any further reduction in price would be ruinous to the planters in a bad season.

On the other hand, the planters, who take a more sanguine view than the Commissioners, consider that by improved culti-

<sup>1</sup> An interesting discussion of this point will be found in a paper by Dr Levinstein (see *Jour. Soc. Dyers and Colourists*, 1901, p. 138).

vation and mode of extraction and manufacture, a greatly increased yield will enable them to place a much improved article on the market at a cheaper rate. This side of the question is well argued in Mr Rawson's paper, read before a meeting of planters and merchants in Calcutta, and abstracted in the *Journal of the Society of Dyers and Colourists* (1901, p. 103).

Under the title of "The Downfall of Natural Indigo," Professor Armstrong, on 15th April, published a long letter in the *Times* discussing Dr Brunck's lecture. He takes it pretty much for granted that the indigo industry is doomed to rapid extinction, and makes this a text for a vigorous attack on the supineness of English business men in regard to the adoption of scientific methods and scientific assistance.

In a letter to *Nature* on "Indigo and Sugar," Dr F. Molwo Perkin also pertinently asks, in reference to the above-quoted figures of the staff at the Badische works, if there "are 148 scientific chemists employed by manufacturers in the whole of the United Kingdom?"

The present crisis in the indigo industry may possibly benefit others indirectly by inducing them to take advantage, more fully than has been the case in the past, of scientific, and therefore rational and economical, methods of manufacture.

XIII.: 1902

APPLIED CHEMISTRY, ENGLISH  
AND FOREIGN

BY SIR J. DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Abstract from Presidential Address, British Association, Belfast, 1902)

THE diplomatic and consular reports published from time to time by the Foreign Office are usually too belated to be of much use to business men, but they sometimes contain information concerning what is done in foreign countries which affords food for reflection. One of these reports, issued a year ago, gives a very good account of the German arrangements and provisions for scientific training, and of the enormous commercial demand for the services of men who have passed successfully through the universities and Technical High Schools, as well as of the wealth that has accrued to Germany through the systematic application of scientific proficiency to the ordinary business of life.

Taking these points in their order, I have thought it a matter of great interest to obtain a comparative view of chemical equipment in this country and in Germany, and I am indebted to Professor Henderson of Glasgow, who last year became the secretary of a committee of this Association of which Professor Armstrong is chairman, for statistics referring to this country, which enable a comparison to be broadly made. The author of the consular report estimates that in 1901 there were 4500 trained chemists employed in German works, the number having risen to this point from 1700 employed twenty-five years earlier. It is difficult to give perfectly accurate figures for this country, but a liberal estimate places the number of works chemists at 1500, while at the very outside it cannot be put higher than somewhere between 1500 and 2000. In other words, we cannot

show in the United Kingdom, notwithstanding the immense range of the chemical industries in which we once stood prominent, more than one-third of the professional staff employed in Germany. It may perhaps be thought or hoped that we make up in quality for our defect in quantity, but unfortunately this is not the case. On the contrary, the German chemists are, on the average, as superior in technical training and acquirements as they are numerically. Details are given in the report of the training of 633 chemists employed in German works. Of these, 69 per cent. hold the degree of Ph.D., about 10 per cent. hold the diploma of a Technical High School, and about 5 per cent. hold both qualifications. That is to say, 84 per cent. have received a thoroughly systematic and complete chemical training, and 74 per cent. of these add the advantages of a university career. Compare with this the information furnished by 500 chemists in British works. Of these only 21 per cent. are graduates, whilst about 10 per cent. hold the diploma of a college. Putting the case as high as we can, and ignoring the more practical and thorough training of the German universities, which give their degrees for work done, and not for questions asked and answered on paper, we have only 31 per cent. of systematically trained chemists against 84 per cent. in German works. It ought to be mentioned that about 21 per cent. of the 500 are Fellows or Associates of the Institute of Chemistry, whatever that may amount to in practice, but of these a very large number have already been accounted for under the heads of graduates and holders of diplomas. These figures, which I suspect are much too favourable on the British side, unmistakably point to the prevalence among employers in this country of the antiquated adherence to rule of thumb, which is at the root of much of the backwardness we have to deplore. It hardly needs to be pointed out to such an audience as the present that chemists who are neither graduates of a university, nor holders of a diploma from a technical college, may be competent to carry on existing processes according to traditional methods, but are very unlikely to effect substantial improvements, or to invent new and more efficient processes. I am very far from denying that here and there an individual may be found whose exceptional ability enables him to triumph over all defects of training. But in all educational matters it is the average man whom we have to consider, and the average ability which we have to develop.

Now, to take the second point—the actual money value of the industries carried on in Germany by an army of workers both quantitatively and qualitatively so superior to our own. The consular report estimates the whole value of German chemical industries at not less than fifty millions sterling per annum. These industries have sprung up within the last seventy years, and have received enormous expansion during the last thirty. They are, moreover, very largely founded upon basic discoveries made by English chemists, but never properly appreciated or scientifically developed in the land of their birth. I will place before you some figures showing the growth of a single firm engaged in a single one of these industries—the utilisation of coal tar for the production of drugs, perfumes, and colouring matters of every conceivable shade. The firm of Friedrich Bayer & Co. employed, in 1875, 119 workmen. The number has more than doubled itself every five years, and in May of this year that firm employed 5000 workmen, 160 chemists, 260 engineers and mechanics, and 680 clerks. For many years past it has regularly paid 18 per cent. on the ordinary shares, which this year has risen to 20 per cent. ; and in addition, in common with other and even larger concerns in the same industry, has paid out of profits for immense extensions usually charged to capital account. There is one of these factories, the works and plant of which stand in the books at £1,500,000, while the money actually sunk in them approaches to £5,000,000. In other words, the practical monopoly enjoyed by the German manufacturers enables them to exact huge profits from the rest of the world, and to establish a position which, financially as well as scientifically, is almost unassailable. I must repeat that the fundamental discoveries upon which this gigantic industry is built were made in this country, and were practically developed to a certain extent by their authors. But in spite of the abundance and cheapness of the raw material, and in spite of the evidence that it could be most remuneratively worked up, these men founded no school and had practically no successors. The colours they made were driven out of the field by newer and better colours made from their stuff by the development of their ideas, but these improved colours were made in Germany and not in England. Now, what is the explanation of this extraordinary and disastrous phenomenon? I give it in a word—want of education. We had the material in abundance when other nations had comparatively little. We had the capital, and we



had the brains, for we originated the whole thing. But we did not possess the diffused education without which the ideas of men of genius cannot fructify beyond the limited scope of an individual. I am aware that our patent laws are sometimes held responsible. Well, they are a contributory cause ; but it must be remembered that other nations with patent laws as protective as could be desired have not developed the colour industry. The patent laws have only contributed in a secondary degree, and if the patent laws have been bad the reason for their badness is again want of education. Make them as bad as you choose, and you only prove that the men who made them, and the public whom these men try to please, were misled by theories instead of being conversant with fact and logic. But the root of the mischief is not in the patent laws or in any legislation whatever. It is in the want of education among our so-called educated classes, and secondarily among the workmen on whom these depend. It is in the abundance of men of ordinary plodding ability, thoroughly trained and methodically directed, that Germany at present has so commanding an advantage. It is the failure of our schools to turn out, and of our manufacturers to demand, men of this kind, which explains our loss of some valuable industries and our precarious hold upon others. Let no one imagine for a moment that this deficiency can be remedied by any amount of that technical training which is now the fashionable nostrum. It is an excellent thing, no doubt, but it must rest upon a foundation of general training. Mental habits are formed for good or evil long before men go to the technical schools. We have to begin at the beginning : we have to train the population from the first to think correctly and logically, to deal at first hand with facts, and to evolve, each one for himself, the solution of a problem put before him, instead of learning by rote the solution given by somebody else. There are plenty of chemists turned out, even by our universities, who would be of no use to Bayer & Co. They are chock-full of formulæ, they can recite theories, and they know text-books by heart ; but put them to solve a new problem, freshly arisen in the laboratory, and you will find that their learning is all dead. It has not become a vital part of their mental equipment, and they are floored by the first emergence of the unexpected. The men who escape this mental barrenness are men who were somehow or other taught to think long before they went to the university.

To my mind, the really appalling thing is not that the Germans have seized this or the other industry, or even that they may have seized upon a dozen industries. It is that the German population has reached a point of general training and specialised equipment which it will take us two generations of hard and intelligently directed educational work to attain. It is that Germany possesses a national weapon of precision which must give her an enormous initial advantage in any and every contest depending upon disciplined and methodised intellect.

XIV.: 1903

## THE RELATION BETWEEN SCIENTIFIC RESEARCH AND CHEMICAL INDUSTRY

BY PROFESSOR R. MELDOLA, F.R.S.

(Lecture delivered at the Oxford Summer Meeting, August 1903)

*THIS lecture deals in a general manner with the interdependence of science and industry, using as illustrations the manufacture of optical glass, fertilisers, the fermentation industries, and the coal-tar colour industry. The fundamental necessity of both pure and technical research is insisted upon.*

XV.: 1905

## THE HISTORY OF THE COAL-TAR COLOUR INDUSTRY BETWEEN 1870 AND 1885

BY PROFESSOR R. MELDOLA, F.R.S.

(Abstract of a Memorandum which accompanies the Report of the  
Committee on Industrial Alcohol: *Journal of the Society of Dyers  
and Colourists*, 1905, p. 175)

THE chief dyes made in England during the period 1870-1885 were magenta, aniline blue, its sulpho acids and by-products, Hofmann violets, iodine green, Bismarck brown, aniline yellow, indulines, phosphine, safranine, chrysoidine, naphthol orange and other azo dyes, picric acid, Manchester yellow, alizarin. During the same period the dyes made abroad, in addition to the above colouring matters, were methyl violet, crystal violet, etc.; methylene blue, acid magenta, malachite green, brilliant green, Victoria blue, night blue, auramine, etc.; monazo colours from homologues of aniline and sulpho acids of naphthols, disazo colours of various kinds, and especially the direct cotton dyes; oxazines, such as gallo cyanine, etc.; phthaleïns. The decline in our coal-tar colour industry began about the year 1880. In 1886 about 90 per cent. of the dyes used in England were of foreign manufacture. The statement that the industry has been driven out of the country for want of duty-free spirit is quite erroneous, because it can be shown that during the earlier years the question of the price of alcohol was quite a subordinate one. Our supremacy had, in fact, been lost long before the price of alcohol, as compared with the prices of the finished products, had become a matter of any great importance. The cost of alcohol as a factor in determining the cost price of dyestuffs could be left out of consideration altogether, but the further back we go into the history of the industry, the less important does the price of

alcohol become. It is perhaps fair to say that during the period anterior to 1870 it was practically negligible, and during the period 1870-1880 it was of quite minor consideration—certainly the relative cost of alcohol at that period does not warrant the belief that our loss of the manufacture had anything to do with the spirit duties.

Beginning with the home list. Hofmann's violet and iodine green are the only dyes into the composition of which the alcohol radical (methyl) enters. They were made from rosaniline and methyl iodide, which was then made from wood naphtha, and was not taxed. None of the other dyes on the list required alcohol in any quantity excepting aniline blue, in which case it was used as a solvent. Methylated spirit was used, and afterwards recovered with little loss. The conclusion seems to be inevitable that the spirit duty had nothing whatever to do with the matter. Hofmann's violet is now extinct, but aniline blue and its derivatives are still important products, but we have lost our supremacy, and by far the largest proportion of these dye-stuffs now on the market is of foreign manufacture. We lost ground, therefore, in a branch of manufacture which was supreme in this country, and for which, although alcohols were required, no excuse for our decadence could possibly have been based on the plea that the spirit duties were to blame. Alizarin, one of the most important products, was at one time manufactured by Perkin's firm and their successors, and afterwards by the British Alizarin Company. Although the raw material anthracene is produced in large quantities in this country, the manufacture of alizarin here became practically extinct for many years, although it is now being restored. Whatever may have been the causes of our temporary decadence in this case, the success of our competitors cannot possibly be attributed to their command of duty-free spirit, because alcohol is not used.

The proximate causes of our decadence, so far as these are concerned with the alcohol question, may be said to be the discovery of new colouring matters and processes by foreign chemists, and the improvement of the processes for manufacturing the products already in existence. The want of duty-free spirit in regard to these improved processes cannot have been great during the period 1870-1885. The introduction of new dyestuffs is, however, of fundamental importance. Coming to the foreign list, with the exception of the oxazines all these compounds were discovered by

foreign chemists. The author discovered the first member of the oxazines in 1879, but it was not manufactured here until many years later, and then not in the factory where it was discovered. The manufacture was at once taken up in Germany. In this case, although one of the raw materials contains the radical of methyl alcohol, the duty upon pure wood spirit had nothing to do with the transference of the manufacture of this colouring matter.

The introduction in 1866 of methyl violet (Poirrier) first created a demand for dimethylaniline which contains the radical methyl. Dimethylaniline was also necessary for methylene blue (1876), malachite green (1878), crystal violet, Victoria blue, and auramine (1883). Diethylaniline was necessary for brilliant green (1879) and night blue (1883). At the time, therefore, when the decline of the industry had seriously set in, with the exception of methyl violet, none of the dyestuffs on the foreign list were made in this country, and the dimethyl and diethylanilines were being manufactured abroad for the manufacture of dyes discovered by foreign chemists. The effect of these newer colouring matters upon the dyestuffs being made here at the time of their introduction is evidently connected with the loss of our supremacy. Hofmann's violet was gradually replaced by methyl violet, and iodine green, which, however, was only produced in limited quantity, was rapidly extinguished by the malachite green group. Victoria blue and methylene blue did not seriously interfere with our aniline blue group, as they fulfilled a different function in the tinctorial industry. In 1880, therefore, the only one of our dyestuffs directly affected by the introduction of dimethylaniline was Hofmann's violet. To what extent did the command of duty-free alcohol give our competitors an advantage in the manufacture of such dyestuffs as methyl violet, methylene blue, and malachite green? They were all foreign patents. When methyl violet was made here the patent had lapsed, the dimethylaniline being imported from abroad, as its manufacture was not taken up here down to 1885, in spite of Government concessions in regard to duty-free alcohol when the point was first raised in 1880. Dimethylaniline can be made by heating aniline hydrochloride with pure methyl alcohol in autoclaves which were used on the Continent at this time, but not here. It can also be made by the action of methyl chloride, obtained in 1878 from trimethylamine, a beet sugar by-product, upon aniline. It therefore could not be produced cheaply in England. At that period

all the coal-tar colours were commanding such prices that the cost of the alcohol was insignificant as compared with the margin of profit. Methyl violet displaced Hofmann's violet because it is made directly from its raw material, whereas Hofmann's violet has to go through several reactions, including the use of methyl-iodide.

With the exception of methyl violet, every one of the new products necessitated the manufacture of some new raw material, such as benzoic aldehyde for malachite green, phenylnaphthylamine for Victoria blue, tolylnaphthylamine for night blue, etc. None of these raw materials required alcohol for their production. The difference in cost between the dyestuffs made from duty-paid or duty-free alcohol, as compared with the margin of profit, was quite insignificant. During the period dealt with our industry was seriously affected by the inventive activity of the foreign manufacturers, but its decline cannot be attributed to their having the use of duty-free alcohol.

The conditions have changed since 1885. Prices were falling from 1880, and the margin of profit becoming smaller. The difference in the cost of manufacture due to the use of duty-free spirit would now bear a very much larger ratio to the margin of profit, and whereas this difference was formerly for all practical purposes a negligible quantity, it may now have become a serious factor. For this reason the author's opinion is that it is desirable that our chemical manufacturers should be placed upon the same footing as their foreign competitors so far as concerns the use of duty-free alcohol.

## XVI.: 1906

### NOTE ON THE PERKIN JUBILEE

To mark the fiftieth anniversary of the discovery of the first coal-tar dyestuff and as a personal tribute to Sir William Perkin, an international meeting was held at the Royal Institution, London, on Thursday, 26th July 1906.

Special representatives were present from Germany, Austria, France, Belgium, Holland, Switzerland, Italy, Denmark, Russia, and the United States, in addition to a very representative gathering of British chemists, and a large number of addresses were presented to Sir William Perkin from British and Foreign chemical and other societies, universities, etc.

A further celebration was held in the autumn of the same year when Sir William Perkin visited the United States.

Many interesting references dealing with the history and development of the coal-tar colour industry will be found in the speeches delivered and addresses presented on the occasion of the London and New York celebrations, but they cannot usefully be summarised here.

A full report of the whole of the proceedings was published in book form by the Perkin Memorial Committee and issued by *The Times Office*, London.



XVII.: 1908

## PERKIN OBITUARY NOTICE

BY PROFESSOR R. MELDOLA, F.R.S.

(*Journal of the Chemical Society*, 1908, p. 2214)

*THIS lecture constitutes the Obituary Notice of Sir William Perkin contributed to the Chemical Society. It gives a complete review of Perkin's life and work, but the points of especial interest from the point of view of the present work are largely covered by the following papers:—*

*Perkin: "The Colouring Matters produced from Coal-tar,"*  
*p. 75.*

*Perkin: "The Origin of the Coal-tar Colour Industry,"*  
*p. 141.*

*Meldola: "The Founding of the Coal-tar Colour Industry,"*  
*p. 234.*

XVIII.: 1908

## THE FOUNDING OF THE COAL-TAR COLOUR INDUSTRY

BY PROFESSOR R. MELDOLA, F.R.S.

(Presidential Address to the Society of Dyers and Colourists, 1908 :  
*Journal of the Society of Dyers and Colourists*, 1908, p. 95)

THE late President of the Society, Sir William Henry Perkin, passed away on 14th July 1907, in the sixty-ninth year of his age, and in the zenith of his fame. It would be superfluous to retell here the story of the discovery of mauve, or the influence of that discovery upon the tinctorial industries. The great international gathering of 1906, which will still be fresh in your memories, furnished ample opportunity for reviewing the life-work of the man whom the nations had assembled to honour, and he himself gave a very full account of his connection with the industry. This is all recorded in the official report of the jubilee meeting published by the Memorial Committee. Some interesting reminiscences were also given by Sir Robert Pullar and others at last year's annual dinner, at which Sir William Perkin presided, and of which a full report was published in the April number of the *Journal*. I have, moreover, written an obituary notice of him for the Royal Society, and in this I have endeavoured to do justice to his scientific work and personal character. It cannot but be a source of the greatest satisfaction to us all—the one mitigating circumstance that lightens our sorrow at his loss—that he fell from our ranks not unrecognised, as is the fate of so many of our scientific pioneers in this country, but laden with freshly bestowed honours, and with the full knowledge that his labours had won lasting gratitude in the two great spheres of human activity, Science and Industry. Further-

more, it cannot but be a gratifying memory to us that our Society throughout its future history will be able to point to the name of Perkin on the roll of its past Presidents. He died in our service, and one of his last acts in connection with this Society was to accompany the deputation to the Dyers' Company in order to plead with that worshipful body for assistance in founding prizes to be awarded by our Society for the solution of technical problems connected with the industry.

On the present occasion our annual gathering, saddened by the loss of our late President, will be made memorable by its marking the first award of the Perkin medal, founded in 1906 in celebration of the jubilee of the discovery and manufacture of the first coal-tar colouring matter. No more fitting tribute to the memory of my distinguished predecessor could be paid than that his successor in this chair should endeavour to enable you to realise the full measure of our indebtedness to him. I propose therefore to invite you to take with me a retrospective glance into the conditions, scientific and industrial, antecedent to that accidental discovery of 1856, which marked the beginning of the modern revolution in all tinctorial methods. Let us consider, in the first place, the state of affairs with respect to the raw materials required for the manufacture of mauve. These were benzene, nitrobenzene, and aniline.

Benzene, as you are aware, was discovered by Michael Faraday, in 1825, as a component of the liquid obtained by the compression of oil-gas. Twenty years later Hofmann found this hydrocarbon in coal-tar, and proved its presence by preparing from it nitrobenzene and aniline, the latter being identified by the usual tests. The occurrence of benzene in coal-tar was thus known in 1845, and in 1848 one of Hofmann's brilliant young students at the Royal College of Chemistry, Charles Blachford Mansfield, at the instigation of his illustrious master, undertook a systematic study of coal-tar, with a view to the isolation and identification more especially of the "neutral liquid oils," of which he tells us in his paper published by the Chemical Society in 1849 we had at that time "no precise information." When Mansfield took up this work a few definite compounds were known to exist in this tar, notably naphthalene, which had been isolated by Garden in 1820, and certain acid and basic substances, such as phenol (carbolic acid), aniline (kyanol), quinoline (leucol or leucoline), and pyrole, all of which had been isolated by Runge in 1834. Anthracene,

under the name of "paranaphthaline," was isolated by Dumas and Laurent in 1833, although it is now known that their original analysis, which assigned to this hydrocarbon 15 atoms of carbon, was erroneous. Chrysene and pyrene had also been indicated, but only superficially studied by Laurent in 1837. To the basic constituents picoline was added in 1846 by Anderson.

Such was the state of knowledge when Hofmann set Mansfield to work upon the coal-tar hydrocarbons. The paper embodying his results is entitled "Researches on Coal Tar, Part I.,"<sup>1</sup> and now, nearly sixty years after its publication, it can still be read with interest and profit. Its contents have become historic in connection with the colour industry, and must rank with Runge's celebrated papers of 1834<sup>2</sup> among the most important contributions to tar chemistry that preceded the foundation of that industry.

Even at the time of Mansfield's work no coal-tar hydrocarbon had been utilised as a source of other chemical compounds, tinctorial or otherwise, and he himself, in describing the practical applications of benzene, refers only to its use as a solvent or an illuminant. Perkin's discovery thus created a demand for this hydrocarbon as a raw material in a new industry on a scale never before contemplated. Mansfield's experiments had prepared the way, but there had been no demand for benzene, and the tar distillers could not at first supply it in quantity or in a sufficient state of purity. It is of interest to know that the first supply of this material used by Perkin came from the Scotch tar distillery of Messrs Miller & Co., of Glasgow.

Then came the difficulties connected with the nitration and the reduction of the nitrobenzene to aniline. Here again Mansfield had played the part of a pioneer, but his process was impracticable on the scale now required. Moreover, it was too costly, for it must be borne in mind that the new dye had to compete with the existing vegetable colouring matters, and on 12th June 1856, Messrs Pullar, of Perth, who had been testing the dyeing properties of mauve, had reported to

<sup>1</sup> *Chem. Soc. Quart. Jour.*, 1849, vol. i. p. 244. He gave a general account of his work at a Friday evening discourse at the Royal Institution on 27th April 1849, which was published as a brochure, entitled "Benzole: its Nature and Utility."

<sup>2</sup> *Poggendorff's Annalen*, vol. xxxi. pp. 65 and 513; vol. xxxii. pp. 308 and 328.

Perkin that the discovery was a valuable one provided it did not "make the goods too expensive." It is needless to say that nitric acid of the strength used by Mansfield would have been a very costly material in 1856. In fact, nitric acid of sufficient strength to nitrate benzene could not be obtained in quantity at that period, and Perkin had to devise apparatus for nitrating with a mixture of sulphuric acid and sodium nitrate. His resourcefulness is well revealed by this passage quoted from his Hofmann Memorial Lecture in 1876:—"At this time neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be, as the kind of apparatus required, and the character of the operations to be performed, were so entirely different from any in use that there was but little to copy from.

"In commencing this manufacture it was absolutely necessary to proceed tentatively, as most of the operations required new kinds of apparatus to be devised and tried before more could be ordered to carry out the work on any scale" (see p. 153, *ante*).

After the manufacture of mauve had been started the demand for the new dyestuff increased to such an extent that the resources of the Greenford factory were taxed to their utmost, and the assistance of another firm had to be called in for supplying raw materials. That firm was Simpson, Maule & Nicholson, whose factory was at Locksfields, in the south of London. The Nicholson of the firm was that pupil of Hofmann's already referred to as having been a co-worker with Mansfield, and, under his energetic management, they not only supplied the firm of Perkin & Sons with some of the raw materials required, but later they also entered the colour industry, and in 1865 established the Atlas Works at Hackney Wick, the firm being transferred in 1868 to Messrs Brooke, Simpson & Spiller. Mr William Spiller, formerly of this latter firm, has told me that he well remembers the early stages in the manufacture of nitrobenzene by their predecessors at Locksfields, where he was then working in association with the late Mr E. C. Nicholson. The nitration was carried out in large glass "boltheads" arranged in series, as they had not then discovered that cast-iron vessels could be used. The scale of working was quite small as compared with the modern output

from a large nitrating still, and they experienced the difficulty referred to by Perkin of obtaining a supply of pure benzene. The operation also was somewhat capricious, owing to the want of uniformity in the quality of the commercial "benzole," and to the absence of mechanical stirring. The cheapening of the process by the introduction of cast-iron stills with mechanical stirring gear did not take place until some time after the manufacture of mauve had been commenced in 1857. The plant in use was described and figured by Perkin in his Cantor Lectures, delivered before the Society of Arts in 1868, and has since been refigured in many works on technology, as it is practically the same in principle as that now generally in use.<sup>1</sup>

The next step, the reduction to aniline, had also to be worked out on the manufacturing scale. The laboratory method then generally in use was Zinin's, viz. sulphuretted hydrogen in presence of ammonia, a process obviously impracticable on the large scale. The use of metals, such as tin or zinc, in combination with acids, would have been both costly and unmanageable. Fortunately, however, Béchamp in 1854 had found that iron and acetic acid could be used for reducing nitro compounds, and Perkin, who had been familiarised with this process in Hofmann's laboratory, applied it successfully for the manufacture of aniline.<sup>2</sup> That this was a task of considerable difficulty can be readily understood by those who are familiar with the violence of such "reducing" processes, unless properly controlled. It is, in fact, known that at first serious attempts were made to extract the minute quantity of aniline contained in the coal-tar oils directly by acid washing—a process which, it is needless to say, had soon to be abandoned on account of its cost and the impure state of the product. In the manufacture of aniline from nitrobenzene the firm of Simpson, Maule & Nicholson also co-operated with Perkin & Sons, and Mr William Spiller has given me a graphic description of their

<sup>1</sup> A workman, James Underwood, in the employment of Simpson, Maule & Nicholson, at Locksfields, during the early years of the colour industry, also remembers this manufacture of nitrobenzene in boltheads and the development to cast-iron stills. This last improvement is generally attributed to E. C. Nicholson. A figure of the earliest form of (horizontal) still was given by Perkin in his Cantor Lectures above referred to.

<sup>2</sup> "Had it not been for this discovery the coal-tar colour industry could not have been started."—W. H. Perkin, Hofmann Memorial Lecture (see p. 153, *ante*).

early work at Locksfields when starting this branch of the industry. The reduction was carried out in iron vessels with removable still-heads, the vessel being at first uncovered, and the materials, nitrobenzene, iron turnings, and acetic acid, simply stirred up by a rod until the reaction showed signs of starting. The still-head was then immediately clapped on, and a workman mounted guard with water-hose ready to play over the still if the contents gave signs of boiling too violently. The cost of the acetic acid was a considerable item at that time, and they had to make their own acid by heating sodium acetate with sulphuric acid. It was soon found that hydrochloric acid could be used instead of acetic acid, and the introduction of stills with mechanical stirrers put this branch of the manufacture on a sure basis. It is perhaps hardly necessary to point out that the "aniline" of that period was a mixture of homologues, and very impure from the modern point of view.

And so the manufacture of the first of the "synthetic dyestuffs" was started at Greenford Green towards the end of the year 1857, and the genius of the founder had ample scope for exercise. Let it be borne in mind that the raw product obtained by oxidising crude aniline with sulphuric acid and potassium dichromate was what would now be called a "resinous mess." Processes for its purification had to be devised, and here again the resourcefulness of Perkin becomes manifest. With that true scientific spirit which dominated all his work the investigation of his products and processes was always kept going. At first the crude product was collected on filters and washed with water to remove excess of aniline sulphate, then dried and powdered, and extracted with coal-tar "naphtha" until free from resinous impurities, then dried again and extracted with methylated spirit, and the filtered solution distilled until the dyestuff separated out. This method of purification was afterwards improved and cheapened by the omission of the naphtha treatment, as it was found that diluted methylated spirit extracted the colouring matter directly, and left the resin undissolved. The process was finally simplified by boiling out the colouring matter with water alone, and precipitating with an alkali so as to obtain the free base, which was then converted into acetate for use by the dyers.

The discovery and manufacture of mauve, with its train of consequences, must be regarded as constituting but a portion of

Perkin's claim to our gratitude. In starting upon this work he had, against the advice of his illustrious master, Hofmann, broken away from the path of pure science and entered a field in which he was a novice. His whole future was bound up with the success of the undertaking, for his father had placed nearly his entire capital in the venture in order to establish the factory at Greenford Green. There was evidently something more to be done besides placing the new dyestuff on the market. The dyers and printers had to be convinced of its merits and taught how to use it. This task, by no means a light one, had also to be undertaken by Perkin, who, up to that time, had never been brought into contact with the tinctorial industries. It has frequently been mentioned that Messrs Pullar, of Perth, were the first to give encouragement to the young inventor so far as concerned the dyeing properties of mauve. At their instigation it was tried for silk dyeing by Thomas Keith, silk dyer, of Bethnal Green, London, and he also reported favourably. But, as is generally the case with new departures, the step from the experimental to the practical scale was not made without encountering difficulties. It was found that on the large scale the dye "took on" unevenly, and caused a patchy appearance, so that a restraining material had to be added to the bath. The use of the soap bath for silk dyeing was the outcome of Perkin's association with a practical dyer, and Keith's dyehouse was the first in which mauve was used on the industrial scale.

Then with respect to wool and cotton dyeing, the same pioneering work had to be done. Perkin has told us that he and Mr (now Sir) Robert Pullar had independently discovered the use of tannin and a metallic oxide as a mordant for cotton dyeing, and, in conjunction with Alexander Schultz, he had introduced the "insoluble arsenite of alumina" as a mordant. The calico printers in this country did not at first take kindly to the new colouring matter, and Perkin has often told me that the impetus to this most important application of his discovery came from France. It appears that, owing to some technical oversight, the French patent was ineffective, and the French manufacturers accordingly began making the new dyestuff themselves. It was in France, in fact, that the term "mauve" was given. With the well-known skill of the French calico printers beautiful designs in mauve were produced and sent over to this country, and this was more effective than any other cause in



hastening the use of the dye for this purpose over here. Had it not been for this stimulus the success of the new factory would have been doubtful, for Messrs Pullar had reported to Perkin that, in their opinion, unless the new dye could be used by the printers it would be questionable whether "it would be wise to erect works for the quantity dyers alone will require."<sup>1</sup> In summing up this part of his experience Perkin stated in 1896 :—

"Before the aniline purple could be introduced for dyeing woollen and mixed fabrics, some weeks were also spent at Bradford in finding out suitable methods of applying it.

"Thus it will be seen that, in the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but, owing to the fact that it belonged to a new class of dyestuffs, a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, etc. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, etc." (Hofmann Memorial Lecture, *loc. cit.*, p. 609.)

It will be remembered that at our last anniversary dinner, presided over by Perkin, Sir Robert Pullar gave us some of his early reminiscences concerning the attitude of the Scotch calico printers towards the new colouring matter.

The success of the new industry had for its natural consequence the creation of a host of imitators. All kinds of oxidising agents were tried upon aniline and made the subjects of rival patents. The departure from the original patent was in some cases so slight that it is questionable whether in modern patent legislation the inventor's claim would not be dismissed as a "colourable imitation." Tabourin and Franc Bros. claimed aniline hydrochloride instead of sulphate; Beale and Kirkham in England, as well as Scheurer-Kestner, Dépouilly and Lauth, Coblentz, and C. Phillips in France, claimed bleaching powder;

<sup>1</sup> "I distinctly remember, the first time I induced a calico printer to make trials of this colour, that the only report I obtained was that it was too dear, and it was not until nearly two years afterwards, when French printers put aniline purple into their patterns, that it began to interest English printers."—Perkin's Cantor Lectures, Society of Arts (see p. 15, *ante*).

Smith claimed chlorine water, Greville Williams potassium permanganate, Kay manganese dioxide, David Price (attached to the firm of Simpson, Maule & Nicholson) claimed lead peroxide, Dale and Caro cupric chloride, Stark and Guyot red prussiate of potash, and so forth. It is needless to point out that many of the products obtained by these inventors could not have been Perkin's mauve at all, and, as a matter of fact, not one of these rival processes was enabled to compete successfully with the original "bichromate" method. The yield was too small, or the colour too difficult to purify, or the oxidising agent too expensive, although at that time the bichromate cost from 10d. to 11d. per pound. The only one of these processes which gave a good result was Dale and Caro's, but even this could not be worked so economically as the original process.

The introduction of mauve by the founder of and pioneer in this new development in manufacturing chemistry soon led, as you are all aware, to the further discovery of coal-tar colouring matters and to the establishment of other factories. My present theme centres round Perkin's work in this field, and I do not propose to enlarge upon the discoveries of others excepting in so far as they influenced the life of our late President. For about a decade the manufacturing operations at Greenford were carried on successfully, and without any fresh discovery of very great importance, although Perkin's activity in the field of pure scientific investigation never ceased. Magenta was first made industrially by Verguin, in France, in 1859, and the firm of Simpson, Maule & Nicholson soon began to manufacture this on the large scale by the arsenic acid process as well as other well-known colouring matters. Such was the development of the industry that in 1862, the year of the International Exhibition in London, Hofmann gave a Friday evening discourse at the Royal Institution,<sup>1</sup> from which it appears that the definite compounds which had been isolated from coal-tar, and which in Mansfield's lists of 1848 consisted of thirteen, had then risen to about forty. It was for that Exhibition that Messrs Simpson, Maule & Nicholson prepared a crown of magenta crystals (acetate), which Hofmann exhibited during his lecture, the title of which was "Mauve and Magenta." The selling price of the new dyes at that time may be gathered from the circumstance

<sup>1</sup> *Chemical News*, vol. vi. p. 90.

that the purified solid mauve sold for about the same price as platinum, weight for weight, and the vat from which the magenta "crown" had been crystallised contained a weight of the acetate of that base valued at £8000, the crystals adhering to the wire framework of the crown being valued at £100.<sup>1</sup>

The discovery and manufacture of magenta was undoubtedly, after the production of mauve, the most important contribution to the industry made during the decade referred to. This discovery did not at first affect Perkin's operations; mauve still held its own, and in 1859 Perkin's brother Thomas, the business man of the establishment, patented on behalf of the firm a process for making magenta by oxidising crude aniline with mercuric nitrate.<sup>2</sup> This was an improvement upon the original stannic chloride process of Verguin, but it was dangerous, capricious, and expensive, and was very soon displaced by Medlock's arsenic acid process worked by Simpson, Maule & Nicholson, and also, as the result of a celebrated lawsuit, by Messrs Read Holliday & Sons, of Huddersfield. But although Perkin & Sons never made magenta in any quantity, the introduction of this dyestuff led to new and necessary developments in their factory. About five years after the foundation of the Greenford works, Hofmann, who had then enthusiastically entered the field of colour chemistry, found that magenta when ethylated or methylated gave rise to violet colouring matters, the manufacture of which was at once taken up by Simpson, Maule & Nicholson.<sup>3</sup> Hofmann's violets and certain phenylated rosanilines, discovered about the same time by Girard and De Laire, in France, and made here also by Simpson, Maule & Nicholson, soon began to enter into competition with mauve.

<sup>1</sup> Some of the original crystals are now in the possession of Mr William Spiller. A trade catalogue of the firm of Simpson, Maule & Nicholson, placed at my disposal by Dr Cain, shows that in 1866 "pure roseine" was priced at 2s. 6d. per oz.

<sup>2</sup> "Das Zinnchlorid wird durch das Quecksilbernitrat ersetzt, mit dem die Fabrikation auch in Deutschland ihre ersten, kräftigen Wurzeln fasst."—H. Caro, *Ber.*, 1892, p. 1031.

<sup>3</sup> The manufacture of methyl and ethyl iodide on the large scale was a remarkable achievement at the time. When I entered the Atlas Works, in 1877, the Hofmann violets were still being manufactured, and the use of these colouring matters by English dyers continued for more than twenty years after that date. The violet is priced in the 1866 catalogue of Simpson, Maule & Nicholson at 3s. per oz.

It has not, I think, been sufficiently dwelt upon by any of the historians of the coal-tar colour industry that Perkin's pioneering discovery reacted upon itself, for there can be no doubt that the production of aniline on the large scale led to the discovery of processes for the manufacture of magenta, and it was the derivatives of the latter that first began seriously to displace mauve. The discovery by Lauth of colouring matters such as methyl violet, formed by the oxidation of the alkylated anilines and manufactured in France about 1866, brought into the field other competitors with the original mauve. The newer dyes were not so fast as mauve, but they were much more brilliant, and fastness soon gave way to brightness. The practical effect of these later developments made itself felt in the gradual decline in the demand for mauve, the use of which soon became very limited, and finally died out altogether. As a flourishing branch of the colour industry it may be said that mauve did not complete ten years of its existence. But Perkin was enabled to keep the Greenford works going successfully in spite of the adverse influence of the new discoveries and the coming into existence of other factories. He introduced in 1864 a very ingenious method for the indirect alkylation of magenta, which enabled their firm to compete with the other violet colouring matters then in the market. This method consisted in heating magenta base with methylated spirit—afterwards improved by substituting methyl alcohol—and the compound formed from turpentine-oil and bromine in the presence of water. This "brominated turpentine" had long been known to chemists, and had been investigated by Greville Williams, but had never before been used for manufacturing purposes. The dyes thus made were introduced under name of Britannia violet of different shades of blueness, according to the degree of alkylation. It was at first thought that they contained the terpene radicle, although it was afterwards considered that they were of the same type as, if not identical with, the Hofmann violets, so that Perkin had really discovered an indirect method of methylation of a type unknown in chemistry at that time. Perkin's process was very successful, although he was handicapped by having to purchase magenta base, which his firm did not manufacture. But, on the other hand, brominated turpentine was cheaper as an alkylating agent than the methyl iodide used in the manufacture of Hofmann violets.

I will venture to interpolate here a small experience of my own, because it is connected with this same department of the colour industry, and, although the experiments which I am about to describe were carried out thirty-seven years ago, I have never had such a favourable opportunity for placing them upon record. The violet dyes now known to be alkylated rosanilines were at that time being sold at very high prices, and any new process, *i.e.* any process which did not infringe existing patents, would have been of very great commercial value. As a youth I had just then entered the colour industry in the service of Messrs Williams, Thomas & Dower, of the Star Chemical Works, Brentford. In 1870 it occurred to me, in view of Perkin's success with brominated turpentine, to try whether the additive compounds of olefines with bromine were equally effective, and my first experience in manufacturing chemistry was the production of ethylene bromide on the large scale. This part of the process was very successfully carried out, and I have a very vivid recollection of the pride with which I displayed ethylene bromide in Winchester quart bottles, the compound being obtained in almost quantitative yield by passing ethylene from alcohol and sulphuric acid through bromine in a special form of apparatus which I devised for this operation. But, alas! the next part of the process proved a failure. The ethylene bromide did react with the magenta base in presence of methyl alcohol, but the alkylene radicle itself entered the rosaniline molecule—there was no transference of radicle as in Perkin's process, and the ethylenerosaniline turned out to be an insoluble resin of no use as a dyestuff. Fuming sulphuric acid might possibly have saved the situation, but this was before the days of "acid magenta," and nobody then knew that such compounds could be sulphonated.

But to return to the Greenford Green factory. After eleven years' successful working with mauve and certain of its derivatives, the Britannia violets, and a few other dyes which are given in the subjoined list, a new impetus suddenly came through the announcement in 1868 that Messrs Graebe and Liebermann, in Germany, had discovered that alizarin, the colouring matter of the madder plant, was a derivative of the coal-tar hydrocarbon, anthracene, and not, as had formerly been supposed, a derivative of naphthalene. The German chemists found also that the compound could be prepared from anthracene,

and thus was accomplished the first laboratory synthesis of a natural colouring matter. I may perhaps be allowed to quote the following passage from my Royal Society obituary notice :—

“This discovery had a great influence upon Perkin’s career as an industrial chemist, and may indeed be considered to have marked a new phase of his activity in this field. There was no living worker in this country at that time besides Perkin who so completely combined in himself all the necessary qualifications for taking advantage of such a discovery. Imbued with the spirit of his early ambition to produce natural compounds synthetically, with more than a decade’s experience as a manufacturer, with the resources of a factory at his disposal, and, not least, with special experience of anthracene as the very substance upon which at Hofmann’s instigation he commenced his career in research work, it can readily be understood that Graebe and Liebermann’s results should have appealed to him with special significance. The first patented process of the German discoverers was confessedly too costly to hold out much hope of successful competition with the madder plant, requiring as it did the use of bromine. Perkin at once realised the importance of cheapening the process by dispensing with the use of bromine, and undertook researches with this object. As a result, the following year (1869) witnessed the introduction of two new methods for the manufacture of artificial alizarin. In one of these processes dichloranthracene was the starting-point, and in the other the sulphonic acid of anthraquinone, the first being of special value in this country owing to the difficulty of obtaining at that time fuming sulphuric acid in large quantities. The second process, which is the one still in use, had quite independently been worked out in Germany by Caro, Graebe, and Liebermann, and patented in England practically simultaneously by these chemists and by Perkin.”<sup>1</sup>

The demand for another coal-tar hydrocarbon, anthracene, in large quantities and in a state of purity, necessitated further pioneering work. Supplies of the crude material had to be procured, the tar distillers had to be educated in the production of raw anthracene, and factory methods of purification had to be devised. It is unnecessary for me to remind you that all these requirements were met by the science and skill of Perkin, then

<sup>1</sup> The patents are :—Caro, Graebe, and Liebermann, No. 1936, of 25th June 1869, and W. H. Perkin, No. 1948, of 26th June 1869.

a young man just turned thirty years of age. The subsequent development of the artificial alizarin industry is too well known to need recital on this occasion. But there is one point in connection with Perkin's work in this field which must not be forgotten, and that is the great importance of the dichloranthracene process in this country at the outset of the new branch of the coal-tar colour industry. Perkin, in conversation with me, has frequently emphasised this point, and I think it desirable on the present occasion to place once again upon record this chapter in the early history of the alizarin manufacture.

The two processes discovered by Perkin, and referred to in the preceding extract, were the anthraquinone process and the dichloranthracene process. In the first of these the anthracene is oxidised to anthraquinone, the latter sulphonated by heating with strong sulphuric acid to a high temperature, and the sodium sulphonate converted into alizarin by alkaline fusion. The sulphonation by this process yields a mixture of mono- and di-sulphonic acids, and the final product is therefore a mixture consisting of alizarin, anthrapurpurin, and some flavopurpurin. This was the process first tried on the large scale by Perkin, as well as by the German manufacturers. The second process, which was patented here by Perkin a few months after the patenting of the anthraquinone process, viz. in November 1869, sets out from dichloranthracene, which is sulphonated by ordinary strong sulphuric acid and the product submitted to alkaline fusion as before. Now dichloranthracene sulphonates more readily than anthraquinone, and as the product consists chiefly of a disulphonic acid of anthraquinone, the "artificial alizarin" obtained by this process consists mainly of anthrapurpurin, with some alizarin and flavopurpurin. Alizarin, as you are aware, gives bluer shades of colour than anthrapurpurin, so that although for certain purposes where bright red was required the mixture obtained by Perkin's second process possessed an advantage, for the production of the bluer reds the anthraquinone product had the advantage. Perkin met this difficulty to some extent by devising a method for separating his "alizarin" into "blue shade" and "scarlet shade," but this method was not easy to carry out on the large scale, and added to the cost of the final products.

For the first few years the Badische Company, which had acquired the Caro-Graebe-Liebermann patent, worked by mutual arrangement in combination with the Greenford Green factory,

the latter having the monopoly of the English markets.<sup>1</sup> The Germans were using the anthraquinone process almost exclusively, this being, as you are aware, the method still in use. When ordinary English oil of vitriol is used for sulphonating, a great excess of acid is necessary and there is much loss owing to the high temperature, so that the dichloranthracene process from this point of view had the advantage. Moreover, when anthrapurpurin was the main object of manufacture it was found that the product obtained by the dichloranthracene process gave much purer shades than that obtained by the anthraquinone process.<sup>2</sup> It would have naturally occurred to Perkin in working out this last process to try fuming sulphuric acid as a sulphonating agent, and he did so with success; but this method, although giving better results in the way of yield and uniformity of product, was placed at a disadvantage here on account of the cost of the fuming acid. The advantages arising from this method of sulphonating are, I may remind you, an increased yield on account of the lower temperature at which the acid does its work, and a product which consists mainly of the monosulpho acid and which therefore gives chiefly the true "alizarin" on alkaline fusion. Now Germany was, at that time, the only country in which the manufacture of fuming sulphuric acid was carried on, and this gave them a distinct advantage in working the anthraquinone process. Perkin has called attention more than once to the state of affairs in this country during the early life of the artificial alizarin industry, and I cannot do better than quote his own statements:—

"On account of the expense and difficulty in getting Nordhausen sulphuric acid imported into this country—few vessels liking it as a cargo—we commenced working with ordinary sulphuric acid. We usually employed four or five parts of this

<sup>1</sup> The amicable arrangement between the German and English manufacturers was brought about through the mediation of Dr Hugo Müller, F.R.S.

<sup>2</sup> Dr Caro informs me that since 1870 the Badische Company employed also the dichloranthracene process for the manufacture of a special kind of "alizarin," consisting chiefly of anthrapurpurin. It may be pointed out also that, owing to some peculiarity in the internal administration of the German Patent Laws at that time, the rights of Caro, Graebe, and Liebermann could not be secured in certain States, and so other manufacturers took up the artificial alizarin industry and entered into competition with the Badische Company. So far as I have been able to learn, the anthraquinone process was generally employed.



to each part of anthraquinone and heated the mixture to  $270^{\circ}$ – $280^{\circ}$  C. . . . I find we employed this process principally in our works until the middle of June 1870. We then began to work on a larger scale than we had hitherto done with dichloranthracene, and carried both processes on for a time, but finding the latter the more economical, partially on account of the ease with which it yielded the sulpho acids with ordinary sulphuric acid, we employed it almost exclusively after a time, although frequently making colouring matter by the other method.

“The large quantity of ordinary sulphuric acid which had to be employed to convert anthraquinone into the sulpho acids, and the high temperature which had to be used, causing a certain amount of destruction to take place, evidently showed that it was desirable to employ fuming sulphuric acid in this process. In this country we found it costly, but as it was more readily procurable in Germany, the manufacturers there used it. They were afterwards supplied with a very strong fuming acid from Bohemia, containing about 40 per cent. of sulphuric anhydride” (“The History of Alizarin,” *J. Soc. Arts.*, 1879, pp. 24–25).<sup>1</sup>

The same statement was repeated in substantially identical terms in 1896. Referring to the loss of anthraquinone when ordinary sulphuric acid is used, he says:—“The means of overcoming this difficulty was to use fuming sulphuric acid, with which anthraquinone combined at a much lower temperature, but the only acid of the kind then made was the old-fashioned Nordhausen acid. We imported a quantity of this, and, of course, found it to work satisfactorily, but the difficulties and expense connected with the carriage and transport of this substance on account of its dangerous nature—supplied as it then was in large earthenware bottles—made it unsuitable for use in this country.

“The artificial alizarin we first made was produced by the anthraquinone process, the method still used for its manufacture, but the difficulty in preparing the sulphonc acid in those early days just referred to caused us to turn our attention to the second process I had discovered, in which dichloranthracene was used. . . .

<sup>1</sup> The use of Nordhausen acid for the anthraquinone process in Germany began about 1871; the introduction of the stronger acid referred to by Perkin in the above passage is generally attributed to Koch in 1873. Dr Caro informs me that he has been unable to find the authority for this statement.

Without this process the manufacture of artificial alizarin in this country could not have been carried on with much success in the early days of its manufacture" (Hofmann Memorial Lecture, see p. 181, *ante*).

The "contact," or "catalytic," process for producing sulphuric anhydride introduced about the same time in this country by Messrs Chapman, Messel & Co., and in Germany by the late C. Winkler, dates from 1875, so that Perkin's share in the founding of this great industry does not consist only in his having given us the practical methods for realising Graebe and Liebermann's synthesis in the factory, but in having devised a process which, so to speak, enabled the new industry to be nursed through its infancy in this country and without which it would probably not have survived that Continental competition which, as Perkin has told us, first began to make itself seriously felt about the end of 1873.<sup>1</sup> By that time it was fully realised that a complete revision of the plant at Greenford Green had become necessary. It required enlarging and modifying in order to meet the successful competition arising from the development of the anthraquinone process in Germany, and a considerable expenditure of capital would have been necessary to carry out this work. But Perkin, whose ambition it had always been to be able to devote himself to pure science, and whose personal requirements were extremely modest, found that his manufacturing career had by then provided him with sufficient means to enable him to retire, and, rather than incur the responsibility of making a fresh start, he took advantage of the opportunity for withdrawing altogether from the industry. His career as a manufacturer terminated in 1874, the Greenford Green works having then been purchased by Messrs Brooke, Simpson & Spiller, which firm, soon afterwards, transferred them to Messrs Burt, Bolton & Haywood, who shifted the manufacture from Greenford Green to Silvertown, and ultimately from this firm the "British Alizarin Company" was developed and is still at work. Perkin always wished it to be known that he considered the Silvertown works as the lineal descendant of the first coal-tar colour factory.

In this sketch of the founding of the coal-tar colour industry I have necessarily limited myself to the history of the Greenford Green factory. These works would now appear quite insignificant in comparison with any of the great German establishments.

<sup>1</sup> "History of Alizarin," *J. Soc. Arts*, 1879 (see p. 57, *ante*).

Although for the most part fallen into disuse, they were visited with feelings of veneration by a large party of our foreign guests during the Jubilee Meeting in 1906. Their erection in 1857 and their subsequent history had marked an epoch in the annals of applied science, the importance of which was known full well to those who had come to this country to render homage to their founder. The whole output of dyes from these works during the seventeen years that Perkin was connected with them was not very great as measured by modern standards. Nevertheless, it may fairly be said that no single factory established in this country has ever given rise to such world-wide developments, both scientific and industrial. When it fell to my lot to take part in the organisation of the jubilee celebration in 1906, it occurred to me that it would be of interest to place upon record the complete history of the Greenford Green factory as a colour-making establishment, and Sir William Perkin was good enough to prepare for me the following list, which has not yet seen the light of publication :—

THE PRODUCTS MANUFACTURED AT GREENFORD GREEN,  
1857-1873

*Mauve*.—Large quantities manufactured.

*Dahlia*.—Ethylmauveine,  $C_{27}H_{23}(C_2H_5)N_4.HCl$ . Made about the same time as Hofmann's violet [1863]. The colour was much admired, but being very expensive was not largely used. (*Jour. Chem. Soc.*, 1879, vol. xxxv. p. 399.)

*Aniline Pink*.—First found in washings from mauve, afterwards produced by oxidising mauve with lead peroxide. It is parasafraanine. Made about the same time as dahlia. (*Jour. Chem. Soc.*, 1879, vol. xxxv. p. 407.) The researches were made many years before publication.

*Magenta*.—Prepared by mercuric nitrate under a patent in my name; a communication from abroad. It was first obtained in crystals in this way. (*Jour. Chem. Soc.*, 1862, vol. xv. pp. 238-240.) The research was made some years before publication. The process was dangerous and not carried on very long.

*Amidoazonaphthalene*.—Used in a finely precipitated form as an orange, red, or scarlet pigment for calico printing, but not largely.

*Britannia Violet* (various shades).—Made from magenta, the bromine compound of turpentine, and methylated spirit, or,

better, purified wood spirit. At first thought to be a turpentine derivative, but afterwards found to be methylated rosanilines. Made in large quantities.

*Perkin's Green.*—This was an interesting compound made by treating Britannia violet (blue shade) with acetyl chloride. The latter was made in large quantities from phosphorus trichloride and acetic acid. The phosphorus trichloride was made in cast-iron retorts with iron condensers from phosphorus and dry chlorine. The colouring matter was obtained in a crystalline condition, but was not investigated as to its constitution. It was rather extensively used for calico printing when iodine green was too expensive.

*"Alizarin."*—Produced very largely, chiefly by dichloranthracene process. It consisted of anthrapurpurin and alizarin, chiefly of the former. These were also separated and sold as "scarlet shade alizarin" and "blue shade," but we chiefly sold the mixture known as "red shade."

Besides the above we made suitable mixtures of aniline salts, oxidising agents, and copper compounds for the production of aniline black. Also the colouring matters were made into "lakes" by processes of our own for paperhangings and lithographic and other printing inks in considerable quantities.

This list contains what may be regarded as Perkin's direct contribution to the colour industry as a manufacturer. It may not appear very imposing to us now, but we must read into it all that it means in order to appreciate its full significance. Consider the pioneering work in every direction that had to be done in order to accomplish these results. Consider further that they were achieved at the outset by a youth of about eighteen, and brought to a successful termination in seventeen years by a young man thirty-six years of age, and that during the whole of that period, while the factory was actively at work, a continuous stream of scientific research was kept going in his laboratory. Consider also the stupendous consequences of the initiation of this industry, and then you will realise the extent of our indebtedness to the man whose labours in this field I have attempted to give you an account of. I am aware that by many who regard manufacturing industry from a narrowly patriotic point of view Perkin has been censured for withdrawing so soon from the scene of his industrial operations. The reply to this charge is obvious. He had made

a sufficient fortune for his modest requirements, and the seeds which he had sown were developing rapidly in this country. At that time (1874) German competition was only just beginning to make itself felt. The industry was flourishing here, and with respect to France it may be said that within a very short period of the founding of the Greenford Green factory, and especially from the time of the discovery of magenta, the industry was also in a prosperous condition there. How thoroughly this branch of manufacture had its head centre in England during the few years following the opening of the Greenford works may be inferred from the fact that such men as Maule and (especially) E. C. Nicholson, both pupils of Hofmann, had entered the industry; that in Manchester the firm of Roberts, Dale & Co. had secured the services of men like Caro and Martius, who later became pioneers in the German colour-making industry. Or, if we turn to the actual products, we find that, in addition to those emanating from the firm of Perkin & Sons, Simpson, Maule & Nicholson had secured the first really valuable process for making magenta, viz. the arsenic acid process of Medlock; that they had also secured the beautiful process of Girard and De Laire for phenylating magenta so as to convert it into blue and violet colouring matters, and that Nicholson, by his discovery of the method of sulphonation, had developed these into what were for many years the most important of all the coal-tar colouring matters. This firm had also introduced aniline yellow (aminoazobenzene), the precursor of the basic azo dyes, and phosphine (chrysaniline),<sup>1</sup> the first member of the acridine series. They were, moreover, the only manufacturers of the alkylated rosanilines under Hofmann's patent. Then the firm of Roberts, Dale & Co. were making picric acid, and had, through Caro, given to the industry the first induline obtained from aniline yellow and aniline, as well as Manchester brown or Bismarck brown. This firm had also, through Martius, given us the dinitronaphthol known as Manchester yellow. Cyanine, or quinoline blue, the first representative of a group of colouring matters which have since become of great importance as special sensitisers for photo-

<sup>1</sup> In the 1866 catalogue of this firm, already referred to, aniline yellow is priced at 2s., and phosphine at 3s. per oz. The Nicholson blues were, at that time, sold only in solution, the price ranging, according to the brand, from 15s. to 30s. per gallon. Solid "Regina purple" is priced at 15s. per oz.

graphic purposes, was discovered the same year as mauve (1856) by Greville Williams, who was for some time chemist at the Perkins' factory, and who afterwards, with Messrs E. Thomas and J. Dower, started the Star Chemical Works at Brentford. This country may also claim to have been the pioneer, through Crace-Calvert and Lowe, of Manchester, in the technical production of highly purified phenol.<sup>1</sup> The first successful method for printing on the fabric with aniline black was discovered and patented in 1863 by John Lightfoot, of Accrington.

This was the state of affairs during Perkin's connection with the industry, and, superadded to this manufacturing activity, was the supremely important fact that, until 1865, the great master, Hofmann, was among us, and that the laboratory at the Royal College of Chemistry had become a centre of active research in the chemistry of colouring matters which stimulated the industry and supplied chemists for the factories.<sup>2</sup> Nor must it be forgotten that Peter Griess, the founder of diazo chemistry, was working over here during the greater part of the same period. It cannot be said that Perkin abandoned the ship in a sinking condition; on the contrary, she was steaming full speed ahead! For any scuttling that may have afterwards occurred he can in no way be held responsible.

The indebtedness of the colour-making industry to the founder of the first coal-tar colour factory does not, however, begin and end with his career as a manufacturer. The example which he has set us as a man will for all time serve to point the moral that all those qualities which make for success in industrial pursuits—scientific ability and knowledge, inexhaustible patience, perseverance, resourcefulness, and energy—may be conjoined with the highest and best attributes of humanity. Such was the personality of the man whose labours have added lustre to the scientific and industrial history of our country, and whose loss touches us the more deeply as representatives of that special

<sup>1</sup> The state of the industry here and in France five years after its inauguration at Greenford Green can be ascertained from Hofmann's report on the chemical exhibits at the International (London) Exhibition of 1862. It is not going too far to say that during its early years the coal-tar colour industry was essentially English and French.

<sup>2</sup> Hofmann left London in 1865. From that time until the creation of the Chair of Organic Chemistry at Owens College, Manchester, in 1874, to which Schorlemmer was appointed, there was no professorship in this department of the science in this country.

industry which, in its present form, embodies the developed results of his pioneering efforts.

#### ADDENDUM

As the introduction of fuming sulphuric acid played such an important part in the early history of the artificial alizarin industry, I have thought it of interest to append the following account kindly furnished by Hofrath Dr Caro. It may be pointed out that the "contact" process for producing sulphuric acid dates from 1875,<sup>1</sup> and therefore subsequently to Perkin's retirement, so that it was his successors who had the advantage of this new branch of manufacture :—

"Previously to the publication of Clemens Winkler, the entire 'Nordhausen Fuming Sulphuric Acid' was manufactured by John David Starck in Bohemia (in several works near Pilsen), and was largely imported into England. It originally contained about 20 per cent. of the free anhydride. This acid was employed by Perkin in his first experimental manufacture in 1869 for sulphonating anthraquinone, and was afterwards in 1870 exchanged for ordinary sulphuric acid,<sup>2</sup> while we (the Badische Company) commenced at this same period with the ordinary acid and gradually went on increasing its strength by adding fuming acid containing about 24 per cent. of free anhydride. I recollect that in 1873 we used chiefly a mixture of two parts of the said fuming acid with one part of the monohydrate. At the same time we studied carefully the effect of the increased strength of the sulphonating agent upon the separate production of the mono- and disulpho-acids of anthraquinone, and I believe that at the same time (1873) similar experiments were made by all German alizarin makers, particularly by Gebrüder Gessert & Co. at Elberfeld, and that in consequence of the superior results obtained by the action of stronger acid at a correspondingly lower temperature a demand was created for fuming sulphuric acid of greater strengths than hitherto supplied. Thus John David

<sup>1</sup> The patent of Messrs Chapman & Messel is dated 18th September 1875. Winkler's process was described in *Dingler's Polytechnisches Journal* for October 1875. Dr Messel gave a description of their process before the Chemical Society in April 1876, but the paper was not published by the Society.

<sup>2</sup> See Perkin's statement (*ante*) quoted from his "History of Alizarin," 1879.

Starck was led to manufacture the solid fuming sulphuric acid containing about 45 per cent. of the free anhydride. This was, I think, in 1873 or 1874. In 1875 we employed regularly the fuming acid of 45-50 per cent. of anhydride. In 1877 we went further in increasing the energy of the sulphonating action by the employment of fuming acid of from 68 to 72 per cent. of free anhydride, which we prepared by distilling the anhydride from one portion of fuming acid into another portion of fuming acid, containing 45-50 per cent. of free anhydride. We also distilled the anhydride into the sulphonating mixture of anthraquinone with fuming acid. Immediately after the publication of Winkler in 1875 we commenced experimenting with his synthetical process, and, after having many times changed our experimental plant, we succeeded in manufacturing the fuming acid on a very large scale from 1877. At about the same time other manufacturers started the manufacture of fuming acid by the synthetical process."



XIX.: 1908

LETTER FROM PROFESSOR H. CARO TO  
PROFESSOR R. MELDOLA, MAY 1908

*THE following letter from Hofrath Dr Heinrich Caro of Mannheim, formerly chemical director of the Badische Anilin- und Soda-Fabrik, is inserted here on account of its historical interest. It bears the date 29th May 1908, and relates to Professor Meldola's address to the Society of Dyers and Colourists on "The Founding of the Coal-tar Colour Industry" (ante, p. 234). Dr Caro had undertaken to write an obituary notice of Sir William Perkin for the German Chemical Society, but he died before the completion of the work. Professor Meldola's obituary notice from the Chemical Society's Journal (ante, p. 233) was therefore translated and adopted after some curtailment by the German Society ("Berichte," 1911, vol. xliv.). The letter is given in Dr Caro's own words without modification:—*

"MY DEAR PROFESSOR MELDOLA,—Having now over and over again perused your excellent historical account of 'The Founding of the Coal-tar Colour Industry,' which you have so kindly sent to me, I beg to offer to you both the expression of my sincere thanks and of my great admiration. Although the main object of your Presidential Address to the Society of Dyers and Colourists has been to erect an everlasting monument to the memory of Sir William Henry Perkin's *industrial* pioneering work in the field of the coal-tar dyes—thus supplementing your prior address to the Royal Society,<sup>1</sup> in which you so splendidly depicted the life and the *scientific* research work of Perkin,—you have given to the world more than a mere personal and biographical account of the great chemist and manufacturer. In those two joint publications you have embodied such a fulness of historical facts,

<sup>1</sup> Obituary Notice: the Chemical Society's notice comprises both the scientific and technical sides of Perkin's work.

partly as yet unknown, and commented upon by your own authoritative remarks, that your *Perkin Essays* will for ever rank amongst the most valuable contributions to the chemical history of the last fifty years. You must have devoted an enormous amount of thought, time, and labour in order to collect and artistically to arrange the documentary evidence upon which you have erected such a *monumentum ære perennis* worthy of Sir William Henry Perkin and his time.

"I now feel justly afraid to proceed with my own biographical work on Perkin's life, which work is still in its infancy and which I have been unwise to promise to the German Chemical Society. You have already said everything that could be said on the subject of Perkin's life-work, and it will be very difficult, if not impossible, for me to discharge my task without following in your wake and copying your writings. On the other hand, I ought to be very thankful to you for having paved my way.

"You have kindly asked me whether I intend coming to the International Congress of Applied Chemistry in London in 1909. I would certainly like to do so, and to visit once more dear old England and my dear old English friends. If I were only ten years younger! But such unfortunately is not the case. I dare not forget that the sun of my life is setting. With my kindest regards,—I remain, my dear Professor Meldola, yours faithfully,

DR H. CARO."

XX.: 1910

## TINCTORIAL CHEMISTRY, ANCIENT AND MODERN

BY PROFESSOR R. MELDOLA, F.R.S.

(Presidential Address, Society of Dyers and Colourists : *Journal of the  
Society of Dyers and Colourists*, 1910, p. 103)

THE FIFTEEN-YEAR PERIOD, 1870-1885, IN THE HISTORY  
OF THE COAL-TAR COLOUR INDUSTRY, AND ITS LESSONS

IN dwelling upon the strengthening of the bonds between science and industry as one of the most important functions of this and kindred societies, I am prompted by the thought that the realisation of the importance—the vital importance—of this union has not been fully grasped in this country even at the present time. Our industry in the course of its history has furnished abundant illustration of that principle which we as a nation have not thoroughly assimilated—the direct practical bearing of science, even in its highest and most abstract form, upon technical and manufacturing operations. For more than a quarter of a century I have taken every opportunity of emphasising the object-lesson conveyed by the history of that branch of chemical industry which immediately concerns us here—the manufacture of coal-tar products inaugurated in 1856 by my illustrious predecessor in this chair, whose services to that industry formed the subject of my address two years ago. Perkin himself did more than any worker of his time to inculcate that doctrine both by precept and example. It is the spirit of propagandism which encourages me to belabour this somewhat jaded hobby on such an occasion as the present one, when it is my privilege to be able to appeal to a wider public through the representatives of an art that is well to the fore in the utilisation of the resources which science has

placed at its disposal and through the members of a Society which may be congratulated on doing good service to that cause which we all have at heart. So far, however, as I am concerned, the preaching of the doctrine that the development of the coal-tar colour industry is primarily the outcome of scientific research is nothing more than the iteration of ancient history. It is interesting to note in passing that it is considered necessary to restate this fact from time to time with all the air of novelty.<sup>1</sup> But after all, if a principle is true, and if its truth is not generally recognised, it may be desirable to freshen up the public mind from time to time, if only for the purpose of reinforcing a lesson which is in danger of being forgotten. From the opinion recently credited to some Hungarian chemist (said to have been twenty years in an English dye-house), in the organ of the Hungarian Association of Chemical Industry,<sup>2</sup> in which both the facts and their conclusions are distorted in a most remarkable way, it is perfectly clear that there is still scope for reiteration. Fortunately, it is possible for me to support the position which I have always maintained by an appeal to that particularly critical period in the history of the industry when I was connected with it, viz. the period following the Franco-Prussian War of 1870. It was soon after this great European disaster that the Continental manufacturers began to get seriously to work, and some ten years later we in this country and the French manufacturers experienced the first symptoms of serious competition from the introduction of new products resulting from German discoveries. Before 1870 and for a few years subsequently the list of synthetic dyestuffs was a short one. Those made at Greenford Green during Perkin's time (1857-1873) were given in a list published in my last address to this Society (see p. 251, *ante*). The staple products when I first entered the industry in 1870 were magenta and the blues derived therefrom, the Hofmann violets, the Britannia violets of Perkin, Bismarck brown, Manchester yellow, indulines, alizarin, and methyl violet, the latter discovered by Lauth in 1861 and manufactured in Poirrier's factory near Paris. A few minor products, such as phosphine, aniline yellow, aldehyde green, etc., were made by certain firms, but it is unnecessary to swell the list. No good green for dyeing purposes was known, and the so-called "iodine green" was too costly and fugitive to

<sup>1</sup> See *The Times*' "Engineering Supplement," 17th November 1909.

<sup>2</sup> *Ibid.*, 9th February 1910.

be of much use. At the time of my second connection with the coal-tar colour industry, which began in 1877, the old state of affairs was beginning to change—at first slowly, but with increasing velocity—and at the time of my severance in 1885 the change was progressing with such speed that I foresaw the approaching decline of our supremacy in that industry, and did my best on every possible occasion to direct public attention to the existing state of affairs.

Now it happens that the period covered by my own personal reminiscences—say from 1870 to 1885—was the most active in the discovery of new types of colouring matters in the whole history of the industry. I do not mean to say that no new types have been discovered since 1885, or that the actual numbers of individual dyes put on the market since that date may not have been greater than before that date. But it is the discovery of new types or of the chemical constitution of old types which is the scientific achievement which precedes and prompts the industrial development and furnishes the manufacturer with the means of producing new compounds of tinctorial value. With the unravelling of chemical structure comes suggestions for new methods of producing compounds of certain specific types, so that the clue furnished by the determination of the constitution of one compound may lead to innumerable compounds of the same type being made available for tinctorial industry. It may be instructive to recall a few of the more conspicuous cases which occurred during the period under consideration. By way of preliminary introduction it may be well to remind you of the fact that the leading idea which furnished the key to the constitutional formulæ of the organic compounds being dealt with in the colour industry, was the application of what is now called the doctrine of valency to carbon compounds, and especially to benzene and its derivatives, by Kekulé in 1865. That epoch-making idea made its way very slowly in this country, while in Germany it was being rapidly assimilated. I well remember in the early years of my connection with the Chemical Society, that the importance of the new benzene theory was realised by only a very small number of our scientific chemists; by the technical chemists and manufacturers it was openly scoffed at, and those who made use of the new ideas in their writings were jeered at for “knocking about benzene rings.” But if our manufacturers failed to see any connection between an abstract theoretical con-

ception and its practical applications, this was not the case elsewhere, and the examples which I propose to give will show some of the results.

The oldest and most largely made dyestuff in the early days of the industry was magenta or fuchsine, for the full history of which I refer you to the books. This colouring matter had been made the subject of much scientific study by many distinguished chemists, and its chemical composition and mode of formation were well known. But its chemical constitution was a mystery till the year 1878, when the problem was attacked by chemists armed with a new mental weapon and, therefore, capable of looking at the question from a new point of view. That weapon was, of course, the Kekulé theory, which had by that time become part of the mental equipment of every truly scientific chemist, and the chemists who paved the way for the solution of this problem were Caro and Graebe, and the men who finally solved it were Emil and Otto Fischer. It is only necessary to state the bare facts here; they are all recorded in history, but I shall never forget the keen delight with which I first read those memorable papers of 1878-1880, in which the Fischers proved that parafuchsine and magenta were derivatives of the hydrocarbon triphenylmethane and its homologue respectively. This discovery settled a point which had engaged the attention of chemists, from Hofmann downwards, for a period of about twenty years. Turn now to the practical consequences of this purely academic piece of work. The type had been revealed. Others of the older dyestuffs, such as the methyl violet of Lauth, the Hofmann violets, the phenylated blues, etc., were all seen to belong to the same type. Furthermore, a well-known green dyestuff, malachite green, discovered by O. Fischer in 1877 and by Doebner (independently) in 1878—the first direct dyeing green of real value—and a few other greens introduced about the same time or a little later, and all made by the same processes, were proved to be derivatives of triphenylmethane. Then followed the scientific development arising naturally from the Fischers' demonstration, viz. the search, and the successful search, for other methods of building up the triphenylmethane type. Totally new methods were devised and new branches of the industry sprang into existence. In addition to the aromatic aldehyde method of Fischer, we had the so-called phosgene colours, such as the Victoria blues, night blue, crystal violet,

etc., all of which appeared in 1883. In rapid succession there appeared later dyes of the same type in which tetramethyl-diaminobenzhydrol or formaldehyde played the part of condensing agents. I have taken the trouble of compiling some lists (from Schultz's tables), the results of which bring out this chapter of applied chemistry in a very vivid way. Before the Fischers' work, there were on the market, roughly speaking, some twenty dyes of this class. I refer only to the basic dyes or their sulphonc acids. Many of these older dyes were not definite compounds at all, but indefinite mixtures or residues and by-products. Now the manufacture of magenta began on the small scale in France about 1859, so that the twenty dyes (of which only some fifteen can be claimed as definite products) represent a period of activity of nineteen years. From 1878 to 1891, the latest date in Schultz's tables for a colouring matter of this type (Green's ed. of 1894), *i.e.* during a period of thirteen years, twenty-four new colouring matters of this class were introduced, everyone a definite compound and some of them competing with and ultimately displacing some of the older dyes of the same class, which, up to that period, had been the staple products upon which some of our manufacturers here had absolutely depended to keep their works going.

I now turn to another large and important group of colouring matters, the discovery of which belongs to the period with which I am dealing. In 1871, Professor v. Baeyer published the first of a series of papers on some new types of compounds which he had obtained by the condensation of phenols with phthalic anhydride and which he termed "phthaleïns." This, as in the previous case, was at first a piece of purely scientific work. Now, fortunately for that country, Germany had in one of her new colour factories a chemist whose services we in this country had lost—a man whose name will be indelibly stamped upon the history of the development of the coal-tar colour industry. I refer to my old friend Dr Heinrich Caro, of Mannheim. It was he who recognised the technological importance of Baeyer's work, and turned this "academic" chemical reaction into a manufacturing process by his discovery that the substituted phthaleïns were possessed of great tinctorial value. Thus appeared in 1874 the eosins, the bromo-derivatives of resorcin-phthaleïn, and I have a vivid recollection of the excitement with which I first experimented with some of these beautiful new dyes when, somewhat

later, they first found their way to this country. The subsequent history is substantially as before. The principle that substituted phthaleins were dyestuffs had been discovered; further discovery for some years turned upon methods for introducing various substituents into the phthaleins, and the list was rapidly extended. From this discovery of Baeyer's in 1871 there was thus developed another branch of industry, creating a demand for raw materials such as phthalic anhydride and resorcinol, which had never before been made on a large scale. In the meantime, Baeyer and other Continental chemists were slowly unravelling the mystery of the chemical constitution of the phthaleins, and after some years it was shown that they were closely related in type to the triphenylmethane group. It may be of interest to add that the question of the constitution of these compounds is still under investigation, but this is a chapter of modern chemistry. The direct descendants of these earlier substituted phthaleins are the well-known rhodamines, first introduced in 1887.

Another important group of colouring matters belonging to the same period owes its origin to a discovery by Lauth in 1876, viz. that certain diamines when oxidised in the presence of sulphuretted hydrogen gave rise to the formation of violet dyes. At first this also was a purely academic discovery; Lauth's violet never became an important addition to the list of available dyestuffs on account of its cost. But the same year the principle was extended by Caro, with the result that methylene blue was introduced. Here again I have a vivid recollection of the sensation produced in this country by the introduction of a new blue dyestuff. Up to that period all the known blues were phenylated rosanilines. No basic blue soluble in water had ever been available for tinctorial industry. The basic phenylated rosanilines had, on account of their insolubility, to be used in alcoholic solution, and the water-soluble blues were salts of sulphonic acids. The chemical constitution of methylene blue was attacked as a scientific problem by Bernthsen in 1883, and successfully elucidated in a masterly series of researches which bore the usual practical result. New and more advantageous methods of making the colouring matter were discovered, and the original methylene blue was soon followed by a number of new dyestuffs belonging to the same type.

This same eventful period witnessed the introduction of other great groups of colouring matters. It is unnecessary to



restate at length histories which are already upon record. I need only mention naphthol yellow or acid yellow (1879), the oxazines (1879), the indophenols (1881), the new series of azo colours which began with chrysoïdine and naphthol orange (1875-1876), fast red, the Ponceaux, Bordeaux, and Biebrich scarlet (1878-1879), blue black (1882), Congo red, the first of the direct cotton dyes and the first representative of that enormous series of azo colours derived from tolidine, dianisidine, etc. (1884-1885). Then we had the new series of quinoline dyes beginning with flavaniline (1881), and the renewed interest in the safranines and allied colouring matters arising from the researches of Witt and Nietzki, and the consequent introduction of many new dyestuffs belonging to this type beginning with phenosafranine (1878), the eurodines (1879), neutral violet (1880), etc. Safranine, as you will remember, was first recognised among the products of oxidation of aniline (crude) by Perkin in 1861, and his own mauve, the first of the coal-tar dyes, was in later times (1888) proved by Fischer and Hepp to be a member of this same series. Within this same period also falls the discovery of the first method of producing the sulphide colours, which have since become of such great importance and which began, in germ, with the old cachou de laval of Croissant and Bretonière in 1873. So also there remain to be recorded the numerous and important developments in the alizarin group, beginning with alizarin orange (1875), alizarin blue (1878), alizarin blue S (1882), etc., gallein and cœrulein (1878), the first of the hydrazine colours, tartrazine (1884); and sun yellow, the first of the stilbene dyes (1883). And last, and by no means least, we have the first indigo synthesis by Baeyer in 1880, and the second (Baeyer and Drewson) two years later, and the settlement of the constitution of this all-important colouring matter in 1888 by this same master worker.

#### CHEMICAL RESEARCH THE PRIME FACTOR IN THE DEVELOPMENT OF THE COAL-TAR COLOUR INDUSTRY

I have narrated this chapter of industrial chemical history in the barest outline, because the details can be filled in by reference to existing literature. But I have spoken of nothing of which I have not personal recollection, because at that period it was my regular habit to keep myself acquainted, as far as was made

known through the ordinary channels of publication, with what was going on in the colour industry outside our own works, and specimens of the new colouring matters sooner or later found their way into our laboratory. I claim therefore with some confidence that this period of fifteen years was not only, as I have said, a most eventful one, but it may even be permissible to go further and to declare that it was the most critical period in the whole history of the coal-tar colour industry. It was the period which witnessed the introduction of nearly all the chemical types of colouring matters on the market at the present time, and it was, above all, the period which saw the stagnation and the commencement of the decay of the British coal-tar colour industry. A careful examination of the history of this period should therefore furnish lessons of the utmost importance. What does this history reveal? In the first place, the broad fact that there was immense activity in the way of discovery, and in the next place, that the centre of this activity was not in this country. Consider all these new types of colouring matters or every individual dye discovered during the period, and it will be found that our national contribution to the industry was quite insignificant as compared with the foreign and especially the German discoveries. The question of the cause of the decline of the British industry resolves in reality into the question of the cause of the Continental activity.

The answer to this last question has been staring us broadly in the face for over thirty years. It is amazing that there should have ever been any doubt about, or any other cause suggested than the true cause, which is RESEARCH—writ large! The foreign manufacturers knew what it meant and realised its importance, and they tapped the universities and technical high schools and they added research departments and research chemists to their factories, while our manufacturers were taking no steps at all, or were calmly hugging themselves into a state of false security, based on the belief that the old order under which they had been prosperous was imperishable. It is true that when the effects of the new discoveries began to make themselves felt, one or two factories did add a research chemist to the staff, but the number and the means of work were totally inadequate. I happened to be one of them, and so I speak with some practical knowledge of the conditions. We were but a handful of light skirmishers against an army of trained legionaries. What could three or four—say half

a dozen at a liberal estimate—research chemists, working under every disadvantage, do against scores, increasing to hundreds, of highly trained university chemists, equipped with all the facilities for research, encouraged and paid to devote their whole time to research, and backed up by technological skill of the highest order? The cause of the decline of our supremacy in this colour industry is no mystery—it is transparently and painfully obvious. In the early stages of its decadence it had little or nothing to do with faulty patent legislation or excise restrictions with respect to alcohol. The decay of the British industry set in from the time when the Continental factories allied themselves with pure science and the British manufacturers neglected such aid, or secured it to an absurdly inadequate extent in view of the strength of the competing forces.

It has often been asserted that the British colour industry suffered from the imperfection of our patent laws. I am quite prepared to admit that there is some justification for this contention; our patent laws were faulty—they are by no means perfect now—but that is a very different thing from the assertion that the imperfection of the patent laws was the main cause of our decadence. This I never did and never can admit. The history of that fifteen-year period refutes it. I say, and always have said, that it was *primarily* our neglect of science which was responsible for our stagnation, in precisely the same way as it may be said, *per contra*, that it was the appreciation of science which was the cause of the progress of our competitors. Had our factories been creative centres, as were the Continental factories—had discoveries of great industrial value been pouring out of research laboratories here, I cannot but believe that the pressure from within would have forced the hands of the legislature, and would have brought about an amelioration of the patent laws long ago. Instead of attributing the decline of our colour industry to the imperfection of our patent laws, the argument, as it seems to me, may fairly be inverted, and it may be said that the imperfection of our patent laws was largely due to our want of initiative in colour industry.

#### TINCTORIAL ART AS A SCIENCE

But enough has been said to enforce the lesson that the development of that industry which chiefly concerns our Society

is the outcome of scientific research. And what is true for the manufacture of those materials which the dyer and printer have to depend upon is equally true for the development of the processes for applying those materials. Tinctorial art is as legitimately a subject for scientific research as is the discovery of new colouring matters. The processes which go on in the dye vat are still under investigation, and physical and chemical interpretations of results which are of everyday experience to the practical dyer are being sought by many scientific workers pursuing many different lines of attack. This Society will do well to keep in touch with this work, for the study of what may be called the "inner mechanism" of dyeing is bound up with some of the greatest theoretical questions of modern physical chemistry. There is in this field another point of contact between science and industry which it is our duty to keep ever in view. Such purely abstract questions as the nature of the "affinity" between fibre and colouring matter, or the relationship between colour and chemical constitution, which are now engaging the attention of some of the leading chemists of the time, can no longer be ignored by the so-called "practical man." The bearing of this work upon practical procedure, if not immediately obvious, is as certain to make itself felt in the future as were the speculations of Kekulé and the researches of the chemists of his time upon the development of the coal-tar colour industry.

XXI.: 1910

## PATENT LAW IN RELATION TO THE DYEING INDUSTRY

BY A. G. BLOXAM, F.I.C.

(*Journal of the Society of Dyers and Colourists*, 1910, p. 119)

DURING the past thirty years patent law has been of great importance to the dyeing industry, and conversely the dyeing industry has been of great importance to patent law, and the industry and the law have together achieved incidentally a much greater result than their mutual benefit. The whole of organic chemistry has been wondrously advanced by the desire of the maker of dyestuffs on the one hand to obtain monopolies of new colours, and on the other hand to avoid paying royalties under existing patents.

The annexed curve (fig. 3), showing the number of patent specifications relating to artificial dyestuffs of each year during the period 1855-1907, is not without interest.

It was in 1856 that the artificial dyestuff industry had its birth. No doubt picric acid, murexide, and one or two other dyestuffs were made artificially prior to that year; I have not been able to find any patents for their manufacture earlier than 1856; their existence does not appear to have led to any systematic study of how to make new colours, such as has arisen since Perkin's Patent No. 1984, of 1856.

The curve is compiled from the official indexes; the indexer has included two specifications, prior to Perkin's, as relating to artificial dyestuffs. One of these, however, deals with a modified Prussian blue, and the other with a mixture of albumen and a metallic powder.

It was not until Renard Frères patented fuchsine, in 1859 (No. 921/59), that the growth of this type of patent became vigorous. That year produced a crop of ten, as is shown in the curve relating to rosaniline dyestuffs (fig. 4). I should have preferred to draw this curve for aniline dyestuffs generally, but whereas it is pretty easy among the earlier patents to pick out those which may properly be said to deal with aniline dyes, it

### *ARTIFICIAL DYES.*

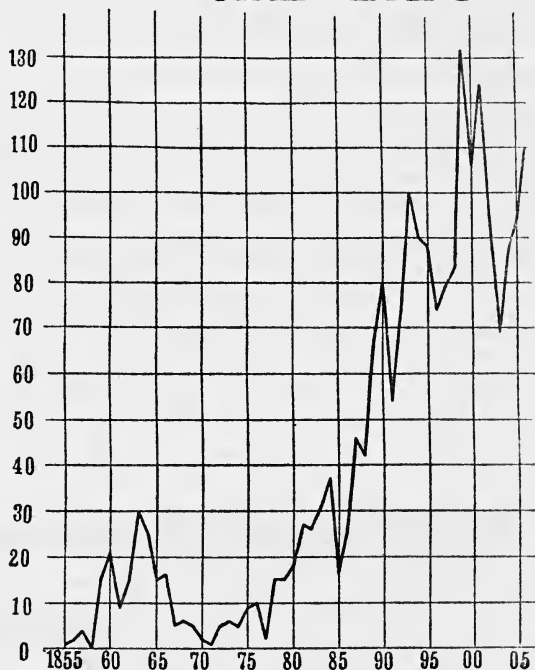


FIG. 3.

becomes almost impossible in later years to make this distinction, because of the great differentiation that has occurred between the numerous descendants of Perkin's patent. The official indexer has classed Perkin's patent in the azine group, so that this patent is not recorded in the rosaniline curve.

The rosaniline curve attained its maximum in 1863, and then declined rapidly, touching zero in 1868 and again in 1872 and 1875. It will be seen that up to this latter year the artificial dyestuff curve and the rosaniline curve are very similar, showing

that for the first twenty years little else was done than the ringing of the changes on aniline and its homologues. The differences between the rosaniline curve and the general curve up to this point are largely due to the anthracene dyestuff curve (fig. 5),

### *ROSANILINE DYESTUFFS.*

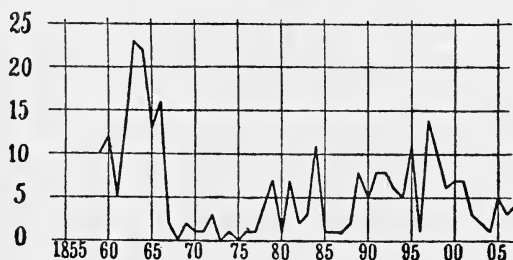


FIG. 4.

which sprang into being with Liebermann and Graebe's Patent No. 3850, of 1868, for the manufacture of artificial alizarin.

There were also a few specifications relating to azo dyestuffs in this period, it having been discovered that by treating amines with nitrites, dyestuffs could be obtained (fig. 6). It was not,

### *ANTHRACENE DYESTUFFS.*

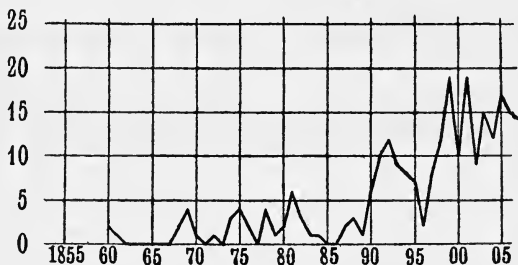


FIG. 5.

however, until Griess's Patent No. 3698, of 1877, that patenting received the fresh blood which it seemed to require. It was in this year also that Germany adopted her celebrated patent law, and it rapidly became the custom to patent in this country all the more important dyestuff inventions patented in Germany.

Turning to the curve of sulphurised dyestuffs (fig. 7), Caro's Patent No. 3751, of 1877, for a dye of the methylene blue class

appears to have been the first, and until 1884 all the dyes thus classified seem to have been of this type. In 1884 Vignon & Co. patented the process of melting paraphenylenediamine with a molecular proportion of sulphur and oxidising the product; several others of this type followed, but it was not until Vidal's Patent No. 9443, of 1894, that sulphurised dyestuffs really made a start. From 1898 to 1899 they jumped from fourteen to forty-six, an increase which it would be hard to rival in any

### ***AZO-DYESTUFFS.***

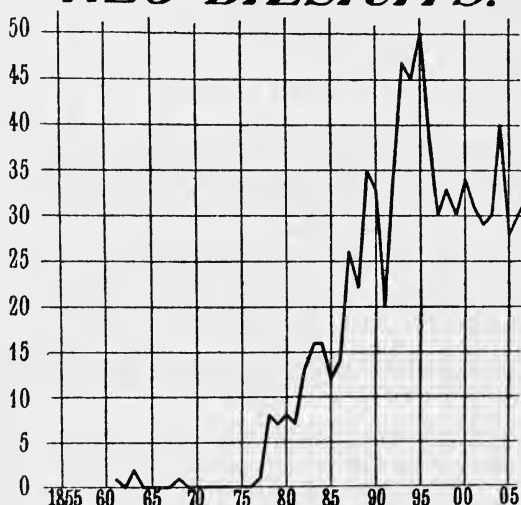


FIG. 6.

subject-matter unless it be the bicycle class; since then, however, they have steadily declined, falling to thirteen in 1907.

1880 was the year of Baeyer's first patent (No. 1177, of 1880) for making indigo. It was from orthonitrophenylpropionic acid, and it did not prove a commercial success. Ten years passed before the Badische Anilin- und Soda-Fabrik patented (Nos. 8726 and 10,509, of 1890) the phenylglycine process, really due to Heumann. Even then patenting did not become general until 1898; it attained its maximum in 1901, and is now on the decline (fig. 8).

These curves, it must be said, only partially represent the activity in the industry. As I have already mentioned, they are limited to specifications which profess to produce the respective



dyestuffs. Intermediate products are not included unless they are described in the same specification as the dyestuff. In the case of indigo in particular this makes a considerable difference

### ***SULPHURISED DYESTUFFS.***

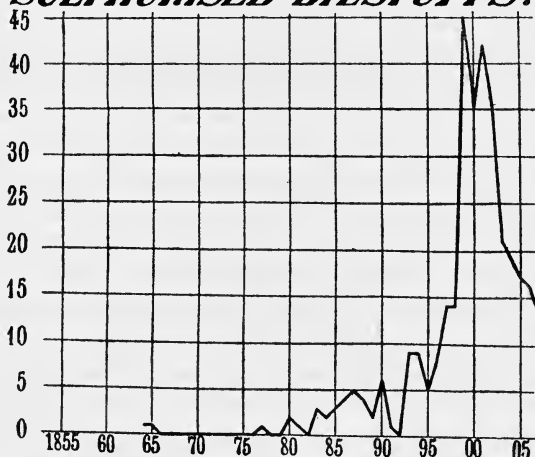


FIG. 7.

in the idea one obtains of the extent of the patenting from a view of the curve ; a large part of the work expended on the subject has been directed to the manufacture of substances destined to be finally converted into the dyestuff.

### ***INDIGO DYESTUFFS.***

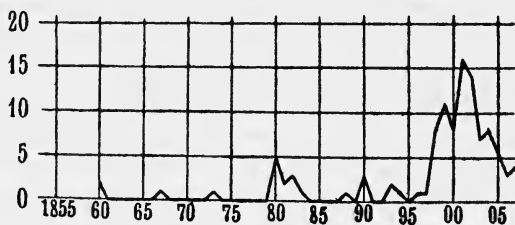


FIG. 8.

The azo dyestuff curve is also rather a poor representation of the activity, although here it is more frequently the case that intermediate products and dyestuffs are described in the same specification. Probably the sulphurised dyestuff curve is most free from this defect, and therefore the much greater number of

patents in this branch is not so remarkable as would appear at first sight.

Prior to 1883 provisional specifications not followed by a complete specification were published, and are included in the curves; subsequent to that date only complete specifications have been published, so that in comparison the number of applications appears smaller.

The maximum of patenting coincides with the maximum of sulphurised dyestuffs, and the heavy decline of the latter during the past ten years has been accompanied by a serious decline in the total number of patents; however, there has been a distinct recovery since 1903, due chiefly to the increased demand for lakes.

The last decade of the nineteenth century was certainly one of marvellous synthetic activity; probably we shall see the like again, but in what direction it is not easy to prophesy. Indigo having succumbed, there does not seem to be any natural dyestuff worthy of sustained attack from the technical standpoint. Some life is at present (1910) exhibited by dyestuffs of the anthracene series, but otherwise the industry may be said to be resting.

It is a matter of some surprise that the manufacturers have been so eager to patent their dyestuffs. Where successful secret working is possible the monopoly may be much longer than that afforded by a patent, and far less troublesome in many respects.

Fortunately for the industry and for science, the manufacturers have preferred to patent; it is sincerely to be hoped that they will continue to do so, for no thoughtful man can fail to realise the immense benefit which must accrue from a system by which inventors are given every encouragement to pour their inventions into the lap of the public, notwithstanding that there is much which the public do not want. Indeed, this must be regarded as the reasonable basis for a patent law.

Abolitionists in respect of patent laws are practically extinct. Switzerland has succumbed, now granting patents not merely for embodied inventions, but for processes. Holland abandoned her fifty-year-old law in 1869, but is now about to legislate again in favour of patents.

It cannot be gainsaid that industry benefits enormously by the publication of inventions; the intended benefit, namely, that the public may know how to exercise the invention at the expiration of the term of the grant, is small compared with the stimulus given to fresh invention, not merely by leading the reader's

mind into fresh fields of thought, but by the desire suggested on the one hand to "go one better," and on the other hand to evade the patent claim. This direct benefit to industry may even be eclipsed by the indirect benefit procured through the educational value of the publication. Patent specifications are becoming our best technical journal, albeit one in which much rubbish is printed.

It is the compulsory and immediate publication as a condition of the patent grant which has led to the present highly developed state of the artificial dyestuff trade and of organic chemistry.

It was largely due to the representations of Mr Levinstein that the Board of Trade appointed a committee at the end of 1900, whose report gave rise to the Patent Act of 1902. This provided a modification of the compulsory licensing clauses (which did not prove satisfactory) and introduced a system of preliminary examination, which came into force on 1st January 1905.

Five years' experience of the working of this system has not caused me to vary my opinion that a preliminary examination is not advantageous either to the public or to the inventor. The system involves a search among specifications to British patents published during a period of fifty years prior to the date of the patent application under examination.

A few years hence, when a considerable number of the patents dated 1905 and onwards have come before the courts, we shall be in a position to judge whether the preliminary examination has had any effect in enabling the patentee to place more reliance upon his patent. I am not hopeful that this will be the case. So far six patents which have been subjected to preliminary examination have been before the courts, and of these only two were upheld as valid.

As I have already stated, patents ought to be granted primarily for the purpose of informing the public how new manufactures are to be conducted. I think there is sometimes a slight confusion of ideas as to the nature of the reward which is supposed to be bestowed on the inventor by the patent grant. I take it that the reward is a recompense to the inventor for *disclosing* the manufacture; it is one which must depend entirely on his own exertions, since the sole profit which he can reap is in working the invention himself or persuading others to work on a royalty. The reward is not one for *establishing* a new industry or manufacture. The difference seems to me considerable; in the one

case the contract between the public and the inventor is that he shall have the sole right to *endeavour* to establish the manufacture and to *continue* the manufacture if established. In the other case, the contract would be that the inventor should have the sole right to manufacture *when* the manufacture had been established. Provisions as to immediate publication would be useless in the latter case, and, indeed, injurious both for the public, as rendering it less likely that the manufacture would be established, and to the inventor, as telling all his competitors in what direction he was endeavouring to obtain the patent reward. Publication would not be necessary until after the establishment of the manufacture, and then only for the purpose of defining the protection afforded by the patent.

The patent grant as a recompense for publication ensures that there shall be no chance of the public losing the increased convenience, comfort, and economy due to the ingenuity of the inventor. At the same time it is inexpedient that the inventor should be allowed to sit on his patent rights, and thus delay the public enjoyment of the fruits of his invention for the whole, or a considerable part, of the term of his patent.

Partly for the purpose of checkmating the dog-in-the-manger patentee, many countries adopted what is known as compulsory working, the patent becoming automatically void after a few years if not worked in the country. This is a very severe measure; the number of patentees who need chastisement for declining to work their patents is relatively very small; the great majority of patentees yearn to have their patents worked, and spend much labour in endeavouring to get them worked. Regarded as a measure against the dog-in-the-manger, this system has never found favour in our country.

On the other hand, the compulsion to grant licences on reasonable terms when requested to do so appears free from objection, and this mode of meeting the objection under consideration has been steadily put forward ever since the beginning of the last century. The difficulty of determining what should be the conditions precedent to the compulsory licence seems to have been the obstacle in the way of the adoption of the mode, and it was not until the Act of 1883 that any provision found its way into our law. The difficulty is not yet settled, however, since the amending Acts of 1902 and 1907 have both varied the original conditions

No system of compulsory licensing or compulsory working exists in the United States. Personally I am disposed to think that the system of compulsory licensing should be carried much further than has been done in any country within my knowledge. Why should it not be incumbent upon the patentee to grant licences to all comers? If he has spent time and capital in setting up a manufacture of the invention before he is asked to grant a licence, this fact must be taken into consideration in settling the royalty. The patentee should have the opportunity of being first in the field; it would be only right that he should not be compelled to grant a licence until his patent was of a certain age. I do not see why the requirements of the public or the public interest—factors which it is always difficult to determine—should come into consideration.

Whatever system of compulsory licensing be ultimately adopted, I am convinced that it will be found an adequate substitute for compulsory working, not only in respect of preventing the patent from becoming a true monopoly, but also in respect of enforcing as far as possible the working of the patent in the country of origin.

To some extent compulsory working is a corollary of protective tariffs. No amount of duty on an imported patented article could serve to establish the manufacture of it if the patentee had the power to veto the manufacture. Even in a protectionist country, however, the policy of penalising non-working by revocation of the patent is suicidal, so far as the establishment of the manufacture is concerned. Those who advocate this penalty are strangely illogical; the patent was granted, they say, to establish a new manufacture because no one will embark capital in such an enterprise without some protection from competition. If the manufacture is not established within a certain period they would proceed to extinguish the sole incentive for establishing it.

At least the revocation should not occur until someone is ready to work the invention. The position would be less absurd if it were essential for the person applying for revocation to show that he is ready to start the manufacture, and has a reasonable prospect of an extensive trade.

To my mind, however, the greatest danger in the system of revocation for not working lies in the fact that it is just the patents which we require most that are most liable to revocation

on this ground. It is the patent which it is difficult to work in this country that is most likely to establish a new industry ; the revocation of the patent will only enhance the difficulty of establishing the new industry. Hence inventors of the more revolutionary inventions will refrain from patenting them until such time as they think there is an opportunity of manufacture being started. This will greatly retard the progress due to early publication and the rivalry already alluded to.

After all, the inventor is granted the patent in consideration of his having *introduced*, that is, *disclosed*, the manufacture, not of his having *established* it. And in practice this is how it happens, almost universally. The inventor gets his reward from the capitalist before the manufacture is established ; it is the capitalist who reaps a reward for having established the manufacture.

If patents are possessed by foreigners in order that they may have a monopoly of importing into this country, the evil—as I will call it, though I am far from convinced that it matters to the country—is remediable by allowing Britishers or other foreigners to obtain easily a licence for importing. If such patents are held for the purpose of preventing manufacture in this country, a compulsory licence will also serve as a cure.

### DISCUSSION

Dr CAIN drew attention to the difficulty of keeping the manufacture of dyestuffs secret, as had been suggested by Mr Bloxam. He mentioned the case of primuline. The manufacturer of this dyestuff declined to take out a patent and decided to keep the process a secret. Being the first of an entirely new class of dyestuffs and, moreover, there being considerable difficulty in ascertaining by analysis its chemical constitution, it was thought that there would be no difficulty in keeping the matter quite secret. Unfortunately, three weeks after the introduction on the English market of this particular colour a similar colour was put on the market by a German firm. He thought that in the case of sulphurised dyestuffs there would be less difficulty in keeping the matter secret. He was of opinion that the cost of applying for compulsory licences for the working of patents in this country was the reason of their not being applied for. With reference to the so-called downfall of the chemical industry in England, he mentioned the fact that Hofmann had often been

credited with the invention of coal-tar colouring matters, to which he was not strictly entitled ; for example, Nicholson prepared a number of products which were handed over to Hofmann. Nicholson by phenylating rosaniline naturally suggested to a chemist the methylating of the same product, the latter producing Hofmann's violet.

Mr W. P. DREAPER defended the British system of chemical training as compared with the Continental, and thought it was more conducive to freedom of thought. In his opinion the number of individual thinkers turned out in England was much greater than was the case on the Continent. He thought that compulsory search was to the advantage of the inventor, as he was thereby enabled to go direct to the Patent Office and not necessarily pass his invention through the hands of an agent.

Dr E. FEILMANN thought that the working of compulsory licences might be settled in a businesslike manner, without calling in the Law Officers of the Crown, the terms being arrived at by the ordinary method of business bargaining, without any interference on the part of paid officers.

Mr BLOXAM, in reply, expressed the opinion that the granting of compulsory licences ought not to be anything like so costly as was the case at present. He pointed out that the average dyestuff patent covered many hundreds of dyestuffs, and it was not necessary to limit the specification to one particular dyestuff, as was the case in the United States. He referred to the fact that in the case of Levinstein, the Board of Trade made an order to grant a licence, but no licence was actually granted.

XXII.: 1910

## THE COAL-TAR COLOUR INDUSTRY OF ENGLAND: CAUSES OF ITS PROGRESS AND RETARDATION

By I. SINGER

(*Journal of the Society of Dyers and Colourists*, 1910, pp. 124-150)

THE question "Why did not the coal-tar industry obtain a sure and permanent footing in the land of its birth, and why has it reached such perfection and development in Germany?" has often been asked and variously answered, according to the standpoint of the critic or the occasion which called forth the reflection.

In this country the high excise duty on alcohol, the patent laws, high wages, the free-trade policy, want of adequate secondary education, the supposed absence of research chemists, have all been mentioned in turn as being concerned in obstructing the development of the colour industry.

In Germany, however, entirely different views prevail. There it is boldly asserted that inasmuch as the coal-tar industry is essentially of a scientific character, it as naturally was bound to become a German industry.

It was to be expected of their patriotism that Germans should accept this explanation as satisfactory and all-sufficient, but it caused no little surprise in other countries where the problem has been discussed with as keen an interest, perhaps, as in Germany itself, albeit it has not been viewed through German spectacles.

This is probably the reason why the editors of the *Vegvészeti Lapok*—the official organ of the Hungarian Association of Chemical Industry—have asked me to state the views entertained



in this country concerning this question. "We know," they wrote, "that the Germans have written a great deal on this subject, but we think it would interest our readers to have an impartial statement of the opinions of the British consumers."

I responded to this appeal with an article which appeared in the Christmas number of the *Vegvészeti Lapok*. I did not attempt, however, to interpret the views of others, but gave my own. In this article, originally intended for Hungarian readers only, I tried to disprove certain allegations which, through persistent reiteration rather than any inherent merits, have gained currency abroad; allegations which ascribed German supremacy in this particular industry to the special aptitude of Germans for scientific pursuits, and, inferentially, affirmed the want of it in this country.

I pointed out not only the inadequacy, but the absurdity of this explanation, and tried to show that the problem itself was neither fairly nor correctly stated, inasmuch as many of the assumed facts could be shown to be untrue or exaggerated.

I hoped the matter would end there as far as I was concerned, but in this I was mistaken. An abstract of my article appeared in the *Chemical Trade Journal* (15th January), and thence found its way into *The Times* (9th February) as an addendum to a contributed article on "Research Chemists." Both these journals were of opinion that my facts and arguments deserved some attention. The *Chemiker Zeitung* of Coethen, however, is of quite the opposite opinion, and is very wroth indeed with the English Press for its indiscretion in taking notice of such abominable heresies, since this compelled them to notice the article themselves.

The most common idea is that England has lost the coal-tar colour industry through want of capable chemists. This opinion finds expression in different forms. Even in this country complaint is made that not sufficient attention is paid to chemical research. The opinion seems to prevail that if more research work were carried on, a larger share of the chemical industries would be secured for this country.

In dissenting from this view, I do not wish to be understood that I intend to disparage research work of any kind. Far from it. The more there is of it the better, provided, of course, that the means could be found to compensate those who would devote themselves to the task.

In Germany they smile at the idea of England ever competing successfully in the organic chemical industries, because, they aver, it is a pursuit which can thrive only in the hands of a scientifically gifted nation. They are quite sincere in believing that they possess special aptitudes for work which requires deep thinking, careful and patient application, and regard the conquest of this industry by Germans for Germany as a crowning proof of "German thoroughness" and "German intellectuality."

This belief was interpreted with sufficient clearness by Dr Duisberg at the Perkin Jubilee banquet in the following words: "No other industry requires so much uniformity of thought and action, science and practice, as organic chemistry or organic-chemical industry. . . . We Germans possess in a special degree this quality of working and waiting at the same time, and of taking pleasure in scientific results without technical success."

I could quote much more to the same effect, but this should be sufficient. Nor would I have noticed this delicious specimen of national self-appreciation were it not that, through constant reiteration, people even in this country have become infected by the belief that Germany has the command of this industry because of her superior education, and that if this country only produced more chemists, she would thereby secure a larger share of the colour industry.

Now it is not necessary to question German genius or German achievements in whatever field of activity, nor to put forth rival claims on behalf of the British people before one may dissent from such opinions.

The most superficial reflection must disclose the absurdity of any suggestion that England has lost the coal-tar industry for want of sufficient acumen, or that the industry owes its present ramifications solely and entirely to German intelligence and industry.

To guard against any possible misunderstanding, I hasten to make clear my meaning. In the above sentence I do not allude to the share of the work which chemists all over the world, and of every nationality, had in making organic chemistry what it is to-day; nor do I intend to belittle the intelligence and industry—admitted and admired the world over—which Germans have displayed in its industrial application. They have worked well; their results are as brilliant as they are well

earned. But what I wish to insist upon is this, that all the intellect and industry of a nation, however great, could not possibly have made the coal-tar industry into what it is to-day but for the inherent potentiality of the germ. As well ascribe the widely diffused application of steam power, of electricity, of railways, or the telephone to the "intelligence and industry" of this or that nation.

In modern organic chemistry and organic syntheses a new principle of wide application has been discovered, and the enormous ramifications of this new industry must be ascribed to this fact, and not to this or that nationality, even though it were—which it is not—the monopoly of a particular race.

Great and rapid as has been the growth of the coal-tar industry, it has not been more so than the spread of, say, electricity, the telephone, the automobile, the typewriter, or any number of industries that might be mentioned. All these have grown rapidly to immense proportions because they supplied a human want, because of their inherent potentialities, and not because of the nationality of the people who were instrumental in their creation.

Nor is it quite correct if—leaving nationality out of the question—we credit the chemists with the creation of this industry, any more than if we credited the electricians with the creation of the electrical industries. At least it is as true to say that these industries have called into being the chemists and the electricians respectively, as that the latter have created the former. The fact is that the chemists and the industry have created and stimulated each other, and the secret cause of their success is the great demand for their products.

This insistence on a clear perception of the basic facts does not in the least lessen the merits of our German confrères; it merely brings the different points involved into their true perspective. The Germans are known for thoroughness in everything they do. They are as intent, as industrious, and as scientific in their shipbuilding, their navigation, their spinning and weaving, as they are in their colour making, and in time may possibly eclipse their British cousins in all these industries. But they have not done so yet. Would it not be absurd to ascribe this superiority in particular industries to greater intelligence in the British, or want of scientific attainment or thoroughness on the part of the Germans?

For it is yet to be proved that more skill, science, or patience is required to make, say, benzopurpurine, than to build, let us say, a Leviathan (with its hundreds of details so carefully adjusted), a Jacquard loom, a combing machine, or that miracle of mechanism—a spinning mule.

It is begging the whole question to say that England has not progressed in the coal-tar industry because she has not the chemists necessary for its cultivation.

Germany did not have them fifty years ago. If she has them to-day it is because the ever-expanding industry has called them into being. And if England has not to-day as many chemists as Germany trained in the organic chemical industries, it is because there is no demand for them. Had they been wanted the supply would have been forthcoming. The nation which produced men like Boyle, Dalton, Davey, Graham, Priestley, Kelvin, Faraday, Darwin, Tyndall, Huxley, Babbage, Arkwright, Stephenson, Watts, Bessemer, Cartwright, Ramsay, Dewar, Perkin, Meldola, and a host of others famous in science, art, and literature, might conceivably have supplied men capable of being taught how to sulphonate a phenol or diazotise an amine—as in point of fact she has done to the full extent of her requirements.

But the contention is too absurd and self-contradictory for serious argument. For by a similar process of reasoning might be proved German incompetency in respect of such arts or industries in which they are excelled by other nations.

Another popular misconception is that England has *lost* the colour industry, or that the industry has retrogressed. Phrases implying one or the other are constantly met with both here and abroad, without anyone ever deeming it necessary to prove such assertions. It is simply stated and accepted as common knowledge. It is a common experience, however, that few things are in greater need of careful investigation and confirmation than the "facts" which "everybody" knows. Most of the assumptions connected with the problem under discussion belong to this class, and should be looked into before acceptance. With this object in view let us look at a few facts which are none the less true because *everybody* does *not* seem to know them. One of these—generally forgotten—is that the crude product, the coal tar, has to undergo many transformations before it becomes a colouring matter, and that at each successive stage of manufacture value is added to the product. Now a large part of these

preliminary and intermediary processes are performed in England on a very extensive scale, and such products have been, and still are, exported to Germany and other countries. That such exports are not negligible quantities may be seen from the following return for last year :—

	British Exports.	British Imports.
	£	£
Raw and intermediary products . . . .	1,630,000	95,000
Sundry coal-tar products (including calcium carbide)	3,007,000	2,319,000
Indigo, synthetic . . . . .	...	117,000
Colouring matters . . . . .	341,000	1,803,000
Total . . . . .	4,978,000 4,334,000	4,334,000
Excess of exports . . . .	644,000	

So that last year the United Kingdom produced £644,000 worth of coal-tar products more than her own not inconsiderable requirements.

This has been true all along the whole period of the coal-tar industry. That is, expressed in money value, this country has always produced more than the value of her own requirements, though some products she imported whilst others she exported.

Let me state here another indisputable fact, though not always remembered by those who talk about the "loss" of the industry, or of its retrogression, and that is that at no time, from the inception of the coal-tar industry to this day, was there any retrogression. Quite the contrary; every succeeding year the total output, whether in coal-tar products generally or in finished colouring matters, was greater than in the preceding year, and is to-day greater than at any previous time.

There can be no question, therefore, as regards the progress of the industry in this country, though that progress may possibly not be comparable to that of Germany.

But even here we are in need of information before we can say that the coal-tar industry as a whole, as distinct from that

of the finished dyestuff, has flourished more in Germany than in this country.

I have no data to prove the contrary, yet I should not admit this contention until some proof were forthcoming. I will state my reasons.

In 1890 Gustav Schultz, in his *Chemie des Stein-kohlen-theers*, gave the following statistics of the quantities of tar distilled for the purpose of colour making in the five principal countries of Europe :—

England	400,000 tons	Germany	65,000 tons
		France	60,000 „
		Belgium	50,000 „
		Holland	15,000 „
		Total	190,000 tons

Thus in 1890 England contributed more than twice as much as all the other countries put together. As already mentioned, this quantity of tar did not leave the country as such, but was worked up into hydrocarbons, bases, acids, sulpho and nitro compounds—in fact, the manufacturing process was pushed on as far as British industrial conditions permitted this to be done profitably. True, none of these fall under the designation of “colours,” but they certainly form an integral and essential part of the “coal tar” industry.

My point is this, that whilst the manufacture of these products has increased, their export has decreased. A private communication to the writer by a member of a firm who are among the largest makers of these products, explains this, as follows :—

“I am very sorry I cannot give you the figures you want with reference to the amount of raw materials exported from England to Germany in recent years, nor the amount of dyes which are returned to this country made from such raw materials. There are no available statistics for either of these figures.

“The export of intermediate and raw products to Germany for aniline-dye manufacture has greatly decreased during the last few years, owing to the fact that a larger proportion of these raw materials is required for use in England. The production of aniline dyestuffs in England has greatly increased, while the production of raw materials has not. In many instances the English works have nothing to spare of raw

materials, where they were formerly anxious to export. A further reason for this diminution is to be found in the formation of the large German combines, who have sought to make themselves entirely independent of the English supplies of raw materials."

Two facts are here confronting us. Germany is less dependent now for her raw material on England, and the exports of such products from this country have decreased. But this does not mean that less of them is produced, for the contrary is the fact. What becomes of them? The answer is partly supplied in the letter I have just quoted:—"A larger proportion of these materials is required for use in England, since the production of aniline dyestuffs in England has greatly increased."

I am aware that the British exports of finished dyestuffs is insignificant as compared with those from Germany. But these sums would not be a true measure of comparison. To these we should have to add the values of domestic consumption, which in England is, of course, incomparably larger than in Germany.

But do not let us lose sight of the main issue through these comparisons. My object is not to contend that England's share in the colour industry is satisfactory. I merely want to show that the past and present agitation having for its object the expansion of this industry is proceeding on wrong lines and in wrong directions, and that because of the many false assumptions.

What then are the actual facts?

1. That this country has a large and flourishing and growing coal-tar industry.

2. That it has also a colour industry, which has never yet lost ground, but has steadily been advancing, and is to-day greater than at any previous period.

3. That England not only more than supplies her own wants in coal-tar *products*, but even in finished dyestuffs consumed the major portion is locally made.

4. That some dyestuffs are produced in this country in larger quantities than in Germany.

5. That whilst some of the colouring matters that have been invented in England are neglected here in comparison with Germany, others that have been invented abroad are successfully manufactured here.

In view of such facts we can no longer allow ourselves to be misled by such questions as "Why has England lost the colour industry?" or "Why has the colour industry migrated from England to Germany?" and so forth. Such leading questions *affirm* far more than they ask and prejudice the whole problem.

It is not a fact that the colour industry has left the country, or that it has lost ground. The truth is that certain parts of the industry have been neglected, whilst others are flourishing.

The matter for inquiry is therefore what *part* of the industry is here neglected, and *why*?

I will endeavour to give answers to these questions and show that England has retained just so much of the coal-tar industry as suited her own peculiar industrial conditions, and rejected or neglected the rest; that she resumed the manufacture of such portions as, in the course of evolution, came within the compass of these conditions; that in this selection and rejection the migration was not all in one direction; and finally, that intellectual superiority or competency on one side or the other has nothing to do with this perfectly natural process of selection.

If we compare the industries which flourish in England with those which have left, or are leaving the country, we shall have no difficulty in arriving at the criteria by which to judge whether a particular industry is congenial to local conditions or not. For it is a great mistake to regard the colour industry as the only one which has migrated from, or had been rejected, partially or wholly, by England in the process of "selection and adaptation."

Most prominent among the factors are undoubtedly the economic conditions. In England wages and salaries are such that an industry which does not lend itself readily to mechanical manipulation and specialisation is, for that reason, more or less unsuitable to the country. From this circumstance follow other considerations, viz. that there must be a sufficient demand for a particular article to warrant an economical outlay on buildings and machinery.

What Mr C. W. Macara, the President of the Cotton Spinners' Association, says of the industry of Lancashire is, in substance, true of every industry in Great Britain.

He says: "The low cost of production is not due to low wages and long hours of labour; wages in Lancashire are higher



and hours shorter than in any cotton-manufacturing district in the world. By wages, I mean what earnings will command in necessities and comforts. The low cost of production is due to an economical first outlay on buildings and machinery ; to highly efficient labour ; to efficient specialisation in the various processes of the industry. . . . In a word, it is due to enterprise, organisation, and skill."

The keynote of all this is specialisation, which presupposes *production on a large scale*. This must not be confounded with a large trade, or a large aggregate turnover. For instance, on the Continent might be found factories many times larger than corresponding ones in England. But they will carry on a multiplicity of processes and produce a miscellany of articles which in England would constitute several distinct trades.

Not only do we have in England "combers," "spinners," and "weavers," as separate trades, but each of these branches is again subdivided according to quality, some works confining themselves to finer and others to coarser qualities of tops, yarns, or cloth. Hence it is that though England is admittedly to the fore in the textile industry, there are certain articles which she cannot compete in—that is, articles for which the demand is too restricted.

And that also is the chief reason why certain branches only of the coal-tar trade flourish in England whilst others are neglected or have been entirely rejected. I say "rejected" advisedly, as being nearer the truth than when it is alleged that the industry has been "snatched" from England.

I will quote two facts in support of this contention. One is to show that even if Germany were to relinquish entirely the colour trade to-day, England would not make a bid for it, save only for such portions as suited her peculiar conditions ; and the other is to show that such portions she either has always possessed or is acquiring in any case.

On the first point I cannot do better than quote Dr Duisberg, although—to do him justice—he drew quite different conclusions from the illustration.

He says : "One of the largest colour manufactories in England had about ten years ago the licence for exploiting all the English patents of two of the largest German colour works, which at that time represented the value of many millions of marks. It did not, however, in any way avail itself of this

advantage, although the English firm had no restrictions and were no worse off than the German ones, as they merely had to pay for this licence a very small portion of their net profits to the patentees for the working of the respective patents.”<sup>1</sup>

In this case therefore it could no longer be a question of inventive faculty, for the colours were invented, their processes worked out, and at the disposal of the English manufacturer, who yet did not avail himself of this advantage. On the other hand, we have—and this is my second illustration—a British Alizarin Company successfully manufacturing an article invented in Germany! Why? The answer seems obvious enough. Alizarin can be made in bulk, whereas “all the English patents of two of the largest German colour works” comprised, on the face of it, a miscellany of articles, representing “the value of many millions of marks” *in the aggregate*, but not sufficient trade in any *single* article to make it into a specialised and paying industry in England.

Phenol, benzol, naphthol, naphthylamine, their nitro and sulpho compounds, etc., are such articles, and they are made and have been made all along in England, not only in sufficient quantity to supply her own wants, but also for export. Alizarin is another such article, and, though invented in Germany, has been successfully manufactured in England all these years.

But let us note here that the British Alizarin Company makes only those brands for which there is a large consumption: alizarin red, alizarin blue, and alizarin orange; whereas in Germany a much greater variety is manufactured. We may, I think, take it for granted that the proportional margin of profit on these three brands is much smaller than on the others of lesser consumption. Yet the firm selected these three and rejected the rest.

Thus restricting itself to what might be called the “bread-and-butter” articles of the alizarins, the British Alizarin Company has, for the last seven years, paid 10 per cent. dividends on a capital of £138,000, and that in a market, be it remembered, which is as open to the German makers as to itself. In view of this should we be justified in assuming that the company does not make the other brands because they are more difficult to produce, or because it has not the chemists at its disposal? I believe the inference that there is not sufficient demand for

<sup>1</sup> Speech at the Perkin Jubilee banquet.

these miscellaneous brands to make them into a paying industry to be nearer the truth.

But—and I wish you to note this point—if a firm does not think it worth while to undertake the production of such articles as are already invented and at its disposal, either freely or against the payment of a percentage on the net profits only, why should such a firm, which exists for profit-making, keep a staff of research chemists to make inventions which it would not know what to do with when made?

I imagine the answer that awaits my question. Germany does so, and makes it pay. But Germany makes many other industries pay which, under present conditions, could not be profitable in England, and *vice versa*.

Again, I would remind you that I am not contending against research work, nor that this or that industry is not worth considering because it does not lend itself so readily to mechanical exploitation. My only object is to point out the facts, so that a remedy might be sought in the right direction. My point is that it is neither the want of research nor shortage of capable chemists that is the reason why certain branches of industry do not flourish here so well as in other countries.

I will give an illustration from my own experience in support of my contention. Let us take three colours that are produced on the fibre :—aniline black, para red, and naphthylamine Bordeaux.

Appropriately enough, all three were invented in England. Any difference there is in their production is in favour of Bordeaux, which is certainly the easiest as well as the cheapest to produce, whilst the black offers by far the greatest technical difficulties. Yet, whilst of aniline black probably more is produced in England than in the rest of Europe put together, only comparatively little is being dyed of the red, and scarcely any of the Bordeaux, though Germany is doing a considerable trade in both the latter colours.

I repeat that were Germany to relinquish the synthetic colour industry to-day, England would make a successful bid only for those portions of it in which the consumption is sufficiently large to warrant the laying down of special plant and on an extensive scale ; and these branches she already possesses.

Alizarin and sulphide blacks—the former invented in Germany and the latter in France—both became British in-

dustries as soon as the market for these articles was sufficient to warrant a profitable outlay for their manufacture. Synthetic indigo is another such article ripening towards eligibility for British manufacture, and would be certain to become in time a British industry, even without the recent patent legislation which impelled the German patentees to start its manufacture in England.

On the other hand, the "two of the largest colour works" mentioned by Dr Duisberg as having unsuccessfully tried to induce an English colour-maker to exploit their patents may, now that they are established in this country, find out for themselves that some articles can be more profitably produced in Germany than in England, even by the Germans themselves.

We may agree therefore with Dr Duisberg in his contention that it would not materially affect England's participation in the coal-tar industry, even if she revised her patent laws. Not, however, because—as he seems to contend—the industry requires talents which the nation is deficient in, but because the industry comprises too many articles of but limited consumption to suit British conditions.

Dr Duisberg is demonstrably wrong in his classification when he assigns to England industries which are purely mechanical and claims for Germany those which require "scientific thought and application." His idea of Englishmen in the arts is as hewers of coal and minders of machines. His words are :—

"Whereas, therefore, the conditions in England for many industries, such as for the mining industry, for spinning and weaving, not forgetting inorganic chemistry, are far more advantageous than in Germany, the latter country has the natural privilege in the organic chemical industry."

There is something patronising in this sentence—especially when, in addition to the hewing of coal and minding of spinning and weaving machines, he suddenly remembers chemistry—inorganic chemistry. He came well-nigh forgetting it, though it represents quite a respectable turnover. For the last year the exports of what is classed under "Chemicals, Drugs, Dyes, and Colours" amounted to over £16,000,000, the imports to £10,000,000, thus leaving a balance of exports over imports of about six million pounds. To this modest sum, however, we would have to add the home consumption, which probably may be as great as that of the rest of Europe put together.

Somehow the eminent German doctor saw the "hands" only

in the British textile mills, and not the brains behind them. He must have been so struck by the ease with which these machines were worked that it quite escaped his notice that they had to be invented, constructed, and improved until they became so automatic that a child could superintend them. Yet those machines can teach an eloquent lesson and illuminate for us the very subject now under discussion. For it was necessity which called those machines into being in a struggle for existence in the strictest sense of the phrase, and the secret of their success is specialisation and the division of labour, the two essential and primary conditions of British industries.

In short, the question whether a particular industry is suitable to English conditions does not depend on its character, whether it is mechanical or chemical, organic or inorganic, requiring much or little skill, but merely whether it is a *bulk industry*.

If you survey the field you will find that in each case where an English firm takes up the manufacture of an article, it is the one with the lowest margin of profit, and therefore the most difficult to compete in. What is it that makes him choose thus? Not the smallness of the profit, nor the ease or difficulty of its production, but the fact—if I may use a slang expression—that there is “something to go at.”

I have dealt with one large feature of the industry only, and have given prominence to it because, though obtrusively present in almost every important industry of the country, it is entirely ignored in the discussion of this subject.

I do not pretend that it is the only reason why the colour industry of this country is not greater than it is, but it certainly is the chief one. Nor do I say that it is right it should be so, that the country should reject every industry which cannot be harnessed to a powerful engine. I only wanted to make clear the fact that the tendency of British industries is towards specialisation, and that, one by one, all those industries which do not lend themselves to this process are being neglected or eliminated.

I could name scores of industries which have left the country, or are in process of leaving, for no other reason; and no amount of research work or inventions can prevent it. You may ask, “Is there no remedy to arrest this?” I believe there is, but not merely by the erection of more universities and laboratories.

You would have to devise means of organising these lesser industries in such a way that they could be exploited profitably.

If a method could be found to do this—and I do not think it impossible or impracticable—the chemists and inventors would come forth without any special creative effort. We are all worried about what to do with our boys. Create the field, and the workers will soon crowd around you. But it is starting at the wrong end to be clamouring for the chemists when you have no use for them.

### DISCUSSION

Dr CAIN wished to correct the statement of Professor Duisberg, which had been quoted by Mr Singer, to the effect that although a British firm of aniline-dye manufacturers had had the opportunity of working in this country the patents of two large German firms, it had not availed itself of that opportunity. He thought there was no secret as to the identity of the parties referred to, and he was able to contradict the statement from his own personal knowledge, and to state that hundreds of tons of dyestuffs had been manufactured in this country under those patents by the firm mentioned.

Mr Singer's attitude with relation to the state of the British aniline-dye industry was entirely opposed to that adopted by the leading authorities, such as, for example, Professor Meldola, Professor Green, and the late Sir William Perkin. These authorities attributed the so-called decline in the industry to the lack of employment of research chemists, and to the general want of education on the part of the manufacturers. He (the speaker) wished to associate himself strongly with these opinions.

Mr Singer's contentions were that there had been no decline in the industry in this country, and if there had it was not due to the cause referred to.

It was probably true, as Mr Singer had stated, that the manufacture of dyestuffs here had gradually increased, and in that sense the word "decline" was not, perhaps, strictly correct, but for all practical purposes it represented the state of the industry as compared with that of Germany. Mr Singer had shown that a consideration of imports and exports did not accurately represent the amounts of dyestuffs manufactured, because it did not take into account the amount, according to Mr Singer a very large one, which was manufactured for home

consumption. He thought, however, that no one would or could deny that roughly about 95 per cent. of the dyes used in England were of foreign manufacture.

That being so, the odd few per cent. could not represent very much. Further, he did not agree with the lecturer's suggestion that British manufacturers would not bother with small manufactures, but would only take up the production of dyes (or other materials) which could be made all the year round with the minimum amount of expenditure on direction and machinery. Mr Singer's illustration of the large quantities of coal-tar products, in particular the cruder products, which were produced in this country, was not a case where the British manufacturer had selected a manufacture especially suitable to the economic conditions referred to. The larger quantity of these products manufactured here, as compared with those furnished by Germany, particularly in the past, was due to the fact that we had always made much more illuminating gas in this country, and, broadly speaking, Germany seemed to have jumped, in the matter of illumination, from lamps to electric light.

There were dozens of dyestuffs, any one of which would keep a large works going continually, but they had not been made here, or, if they had, only to a small extent. What was the real reason of this, and why had not a great dyestuff industry arisen in this country as well as in Germany? The cause was, in his opinion, the lack of education both of the manufacturers and of the people at large. The manufacturer had not in the past really understood his business. He had not kept abreast with scientific discovery, and did not realise the possibilities of such discoveries as applied to his manufactures; consequently he did not see the enormous necessity of employing research chemists. What was true of the individual manufacturer was true also of the investing public. The average investor, he thought, usually fought shy of investing his capital in businesses concerned much with patents or the possibility of taking out patents—he suffered from the practical mind which often meant one deficient in theoretical knowledge. He was incapable of understanding the possibilities of applied chemistry, and consequently capital flowed into other channels. This was not, and had not been, the state of things in Germany. The higher standard of education in Germany had had its effect on both manufacturers and investors, with the result that was seen to-day.

Mr SINGER, in reply, said that his contention was not that England had as large a colour industry as she might or should have, but that the reasons given for this shortcoming were wrong. The prevalent idea seemed to be that England has lost the colour industry for want of scientific equipment. He had disproved this assumption by showing that neither has England lost the industry, nor has the latter retrogressed.

The facts to which he tried to give prominence were : (1) that in this country inventions were disregarded unless or until they related to objects for which there was an ample market ; (2) that failing such condition, an invention would be useless, and hence an increase of the number of persons engaged in the making of such inventions mere waste of time and money ; (3) inventions actually made in this country were locally neglected, whilst others, made abroad, were successfully exploited here. From which he would draw the inference that it was not want of education at all, but the tending towards specialisation, which made mass production a necessary condition.

He would put it to the test, there and then, whether his reasoning had any justification by submitting to his hearers three proposals which everybody could answer for himself. The first would be to form a company for the purpose of employing research chemists with a view of exploiting their inventions. Would anybody subscribe a single sovereign to such a venture as a business speculation ?

His second proposal would be to offer them inventions already made. Having assured themselves of the genuineness and utility of the invention, would not almost their first question be the probable consumption of the article, with a quick calculation whether it was at all worth bothering with ?

But if—as his third—he would put before them a well-considered project, no matter of what kind, which showed a reasonable prospect of a fair return of profits, could it be conceived that such a project would fail for want of talent, scientific or commercial ?

The subject for inquiry was therefore to find out why industries which could not be harnessed to powerful engines are being neglected, or by what means such industries might be organised and made into paying concerns consistent with the economic and social conditions of the country. That is the direction in which a solution of the problem under discussion



must be sought. Dr Cain had stated that he could mention dozens of dyestuffs that would keep a large works going continually, but which had not been made here. He did not doubt it. But would Dr Cain suggest he could not find the men here to make them? Surely not. Whatever may be the cause or causes of the neglect of a particular industry, it cannot be the want of talent, since that is always forthcoming in response to the demand for it. He (the speaker) was at one with Dr Cain in desiring more education and more research work; but he doubted whether these in themselves would advance the colour industry. He was rather inclined to think it was the other way about—that the expansion of the colour and allied industries would, by creating a greater demand for chemists, assist in their creation.

XXIII. : 1914

## THE ARTIFICIAL COLOUR INDUSTRY AND ITS POSITION IN THIS COUNTRY

BY F. M. PERKIN, PH.D., F.I.C.

(*Journal of the Society of Dyers and Colourists*, 10th November 1914, p. 339)

THE coal-tar industry was founded by my father, and in the early stages of the work he received much encouragement from Messrs Pullar, of Perth, particularly from the late Sir Robert Pullar, the father of the present President of the Society. It is doubtful whether, without that encouragement, he would have commenced to manufacture the product he had discovered.

I will in the first place give a brief historical outline of the commencement of the industry, then reasons why it ultimately in a large measure passed to the Germans, and finally how it may be possible, in part at any rate, to resuscitate the industry. The views given are my own opinions, but I give them for what they are worth.

In the Easter vacation of 1856 my father, who was at that time just eighteen years of age, having been born on 12th March 1838, found that when aniline sulphate was acted upon by potassium dichromate a black precipitate was obtained, and on examination the substance was found to be "aniline purple or mauve." This particular work was carried out in a rough laboratory, which he had fitted up in his father's house, known as "King David's Fort," at Shadwell, in East London.

As a matter of fact, the actual discovery of the dye was an accident. The aim which my father had in view was the synthesis of quinine. With our present knowledge we know that it would not be possible to synthesise quinine simply by the oxidation of aniline, but in those days, when organic chemistry was in

its infancy, the assumption appeared quite probable. In 1856 it seemed quite legitimate to assume that a natural product might be synthesised if the elements composing it could be brought together in the right proportions.

Now, although the actual discovery of the dye was an accident, it required a mind of particular aptitude to work up a dirty black substance, to extract the dye, and afterwards to carry out the laborious work which was necessary to prove that it was a dye and could be used in place of dyes obtained from natural products. I wish to lay stress on this, because the average person—the “man in the street”—is apt to think that the discovery of a substance is the main point. It is really not the discovery of a new substance which is the chief thing, for thousands of substances have been discovered which have been put on one side as useless until the inventive mind came along and opened out new branches of industry.

My father, having discovered this unprepossessing black material, instead of throwing it away, experimented and found that a brilliant colouring matter could be produced from it which had the properties of a dye, and which resisted the action of light remarkably well. Samples of silk and cotton were dyed with it and sent to Messrs Pullar, of Perth, who, after examining them, wrote on 12th June 1856 :—

“If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a long time. This colour is one that is wanted in all classes of goods, and could not be obtained fast on silks, and only at great expense on cotton yarns . . . and does not stand the tests that yours does, and fades by exposure to air.”

After further experiments, a patent was taken out (No. 1984, 1856), and it was decided to commence manufacturing. In June 1857 the building of the works was begun. In December of the same year, the technical difficulties of manufacturing nitrobenzene from benzene having been overcome, also the manufacture of aniline on a large scale from nitrobenzene, and finally the oxidation and preparation of the dye, aniline purple, or Tyrian purple as it was then called, was put on the market and used for silk dyeing in the dyehouse of Mr Thos. Keith, of Bethnal Green.

In introducing the new colour, an enormous amount of experimental work had to be carried out. Mordants for use in cotton

printing had to be devised. Many experiments were necessary before satisfactory results were obtained in dyeing wool and silk with this new dye. It was, in fact, all pioneering work from purifying the raw material and devising new plant, to finally applying the new product.

In connection with the raw product—benzol—it is interesting to note that it was manufactured only in small quantities in 1856, and that the price was 5s. per gallon for a comparatively crude product, which had to be distilled before it could be used. The coal tar itself was a drug on the market, and a great nuisance to the gas manufacturer. With the advent of the aniline dyes, and the consequent call for more and more of the products contained in the tar, the conditions changed and by degrees tar-distilling plants were erected, and became a source of profit to the gas manufacturer.

The introduction of a new colour from a novel source naturally attracted a great deal of attention, and as a consequence many workers came into the field and a large amount of research work was carried out with aniline and allied products, and the number of synthetic dyes gradually increased. The second aniline dye, magenta or fuchsine, was discovered in France by Verguin, in 1859, who produced it by heating commercial aniline with tin tetrachloride. In these early days quite a number of British patents were taken out, although of course a great deal of work was being carried on on the Continent. It must also not be forgotten that a large amount of pioneering work was instituted under the direction of the German chemist, Professor Hofmann, at the Royal College of Chemistry, London. In fact, the influence of Hofmann was of enormous value, as he imbued his students with a love of research, and taught them the importance of thoroughness in their work. The Germans, recognising Hofmann's great gifts, ultimately induced him to return to his native land as a Professor at Berlin University.

In the early days of the aniline-dye industry, probably owing mainly to the influence of Hofmann, there were many German chemists in English works, a number of whom returned to Germany and have most materially helped the German colour industry.

My father's works at Greenford Green in Middlesex were the first coal-tar colour works, but quite a number of other works sprang up within a few years. Some of these no longer exist,

but others are still with us and are of considerable size, employing a large number of hands.

A short time after the Greenford Works had been founded, Messrs Simpson, Maule & Nicholson commenced to manufacture dyes, Edward Chambers Nicholson, one of the partners and a student of Hofmann's, being a chemist of high attainments. Simpson, Maule & Nicholson were originally manufacturers of fine chemicals. When mauve was produced, they took up the manufacture of nitrobenzene and then aniline, and gradually developed into manufacturers of dyes, being the first, I believe, to manufacture rosaniline in this country, and producing it in a high state of purity.

Messrs Roberts, Dale & Co. began working before 1860. Levinstein's commenced in a small way in 1864. Read Holliday & Sons, Williams Bros., and Dan Dawson all commenced about 1865. From the first all these firms employed highly trained chemists who, by their research work, did much to place the industry on a strong basis. Many of the chemists, however, were Germans who, as already mentioned, ultimately returned to the land of their birth and, for reasons which will be mentioned later, it was not possible to replace them by men of equal calibre. The names of a few of these German chemists, who did so much valuable work in England, may be mentioned :—Dr Caro, who ultimately became chief chemist to the Badische Anilin- und Soda-Fabrik ; Dr Martius, who was later appointed chief chemist to the Berlin Actiengesellschaft ; Peter Griess, the discoverer of the diazo reaction (chemist to Allsopp's Brewery at Burton-on-Trent) ; and Dr Otto N. Witt, who became Professor of Chemistry at the Charlottenburg Technische Hochschule.

Up to 1875 the British industry was in a flourishing condition, and fairly held its own against foreign competition ; and a very large number of important patents were taken out in this country. For example, Dr David Price, in 1859, patented violine, purpurine, and roseine, which he obtained by oxidation of aniline with lead peroxide. Medlock took out a patent in 1860 for magenta. In the same year, Greville Williams discovered quinoline blue, afterwards known as cyanin. Patents for violets were taken out in 1860 by Dale and Caro, and by Smith and Coleman. In 1862 Perkin patented another series of violets, and in 1863 Hofmann discovered a violet known as Hofmann's violet, which was manufactured by Simpson, Maule

& Nicholson. Aniline black, probably the fastest of all blacks, was discovered by Lightfoot in 1863. It is unnecessary to further enumerate.

A very great stride in organic synthesis was made in 1867 by the German chemists, Graebe and Liebermann, who showed that the vegetable dye, alizarin, could be prepared by fusing dibromo-anthraquinone with caustic potash. They patented this process, but it was far too expensive to be of commercial importance.

My father, when with Hofmann, having had special experience of anthracene, and having kept considerable quantities from the time when he was a student, was naturally much interested that anthraquinone, which is obtained from anthracene, could be converted into alizarin. He therefore studied the matter further, and found that alizarin could be produced by sulphonating anthraquinone with fuming sulphuric acid and then fusing with caustic soda. He also devised another method which consisted in chlorinating anthracene and then treating with sulphuric acid and afterwards with caustic soda. On treating the melt obtained by one or other of these methods with acid, a yellow precipitate was obtained, which dyed madder mordants with the greatest ease.

All the alizarin used had, up to this time (1869), been produced from the root of the madder plant. This then was the first synthesis of a natural or vegetable colouring matter.

At the same time that experiments were being carried out in England, the German chemists, Caro, Graebe, and Liebermann, were also investigating the subject, and discovered the sulphonation process about the same time as Perkin. Although the patents were filed within a day of each other, artificial or synthetic alizarin was first manufactured in this country, and until 1874 the Germans sent very little into the United Kingdom.

In 1868 the amount of madder root produced was estimated at 70,000 tons a year, but in a few years the artificial product almost completely replaced the natural colour, and madder ceased to be grown. The total output of alizarin from the madder root was about 750 tons in 1868, but in 1912 the output of the synthetic product had risen to about 2000 tons, four-fifths of which was manufactured in Germany.

The development of this branch of the coal-tar colour industry was thus described by my father in his Hofmann Memorial Lecture in 1896:—

"Before the end of the year 1869 we had produced 1 ton of this colouring matter in the form of paste ; in 1870, 40 tons ; in 1871, 220 tons ; and so on in increasing quantities year by year. As we had been successful in producing artificial alizarin, others did not run much risk in following our lead ; yet up to the end of 1870 the Greenford Green works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country."

He then went on to say—and the remarks were not only directed to his own work but to the work of other firms, notably Simpson, Maule & Nicholson, who for some years were the largest coal-tar colour producers in the world :—

"From the foregoing it is seen that, as in the case of the aniline colours, all the pioneering work connected with the foundation and establishment of this branch of the coal-tar colour industry was also done in this country.

"For the due development of this industry, it was necessary not only to attend to technical processes, but also to carry on scientific research in connection with it."

*The neglect of scientific research during the next decade was the reason why the coal-tar colour trade, established as it was in this country, gradually got forced out by German competition.*

In 1874 the Greenford Works were sold to Messrs Brooke, Simpson & Spiller, the manufacture of alizarin being taken over at a later date by the British Alizarin Company.

I have seen it in the Press, and have also heard it in conversation, that it was not a very patriotic step to dispose of a successful works at the early age of thirty-six. The reasons for doing so were practically these. My father and his brother had had a very difficult fight to establish the works, and had at last reaped some benefit from their struggle. The use of aniline and alizarin dyes was increasing by leaps and bounds, and their agents all over the country were urging them to increase their output largely. This practically meant doubling the size of the works ; and this again meant that they would have to sink most of the capital which they had made, in bricks, mortar, and machinery. Although my father preferred a quiet life in which to devote himself to research work, the increasing of the works would probably not have been an insuperable difficulty or

prevented him from carrying on the business ; but the necessity of having more trained research chemists, if the works were to be carried on satisfactorily, became increasingly apparent. It was not possible for one brain, however energetic and fertile, to carry out all the necessary research required in a large works. Research chemists, however, could not be obtained. Our universities did not train them. True, Germans could be had at moderate salaries ; but German research chemists, after they had obtained a thorough knowledge of the processes, had a tendency to go back to their own country, where they were received with open arms and offered high salaries by the German companies.

In an industry such as that of the aniline dyes, continual change is necessary. Consequently, a number of highly trained research chemists must be employed, and it is the works which can turn out the largest number of new colours, and at the same time improve the methods of manufacture and the quality of the older ones, which will obtain the market.

This is what the Germans have done. It is not correct to say—except to a limited extent—that they have stolen the artificial colour industry from us. There certainly has been a lot of piracy. In the early days of the industry, German patent laws were, to say the least of it, chaotic, each State either having its own laws or its own ideas as to the administration of the patent laws. Therefore, for all practical purposes, no patent law existed. It followed, consequently, that the Germans had the brains of the world at their disposal and they had to pay no fees for their use. The moment a patent was published it was seized upon by the German firms. If a process was worked secretly, the Germans, either by research work or by other means, discovered it and appropriated it. The products manufactured by them were sent into this country ; it was vain to prosecute their agents, because when the Germans found this was being done they supplied the goods direct to the consumers. They sent their travellers, many of them skilled chemists, all over the world. They were therefore able to show how the dyes were best employed. The British manufacturers were, as a rule, content with issuing circulars to their customers, warning them not to use inferior foreign goods. As a matter of fact, the goods, as a rule, were not inferior to the British, and were often cheaper. It is, however, an undoubted fact that the German colour works,



when they were first founded, stole the work of English brains. The British Government protected their processes by allowing them to take out patents in this country which they were not required to work. On the other hand, German patents were refused to the British inventors. This was the case with the alizarin patents ; they were granted to Germans in England, but refused to Englishmen in Germany.

I do not think that the German competition with alizarin was very serious until after 1874, because, up to that time, it could be manufactured and sold at a good profit at a price which did not admit of much German undercutting. Shortly afterwards the price of the alizarin paste in this country was raised, and this gave the Germans their chance, which they seized with characteristic energy and undersold the English manufacturers. The English policy should, of course, have been in the opposite direction, to keep the price low, particularly as the Germans were getting in a position to supply the whole demand, if they could only obtain the trade. As a matter of fact, by combining together, the German manufacturers for a time practically killed the British alizarin industry, and had it not been for the 'Turkey Red Dyers' Association, who combined to manufacture alizarin, the trade would probably have entirely left the country. At any rate, the Germans have made very great profits, and employed these in the first case to write off their capital expenditure, and secondly to reconstruct and equip their works with magnificent laboratories, staffed with skilled research chemists. The patent laws, until the Bill of 1907 was passed, allowed foreign nations to patent any process in this country simply to prevent us manufacturing, while we, if we patented abroad, must manufacture the product in the particular country in which the patent was taken out within a reasonable period, or else grant a licence.

In 1907 the Patent Laws Amendment Act was passed, in which it was made compulsory for a foreign patentee either to work his patent in this country, or else to be compelled to grant a licence. Unfortunately, many loopholes for evading this Act have been discovered, and it has not been so successful as was anticipated.

With our own patent laws against us, the Germans made the most of it. But the German spy system, of which we have seen so much recently, was also against us. In many cases, however, our want of business method and *always our disdain of research*

*work were against us.* After a process was once started it was, and even to-day is, largely worked by rule of thumb. I grant you there is a stirring amongst the dry bones, yes, a great stirring, but if we are going to take our place in the manufacture of aniline dyes and fine chemicals, the stirring will require to be very much more vigorous, and unless, after being stirred, the bones are going to be jointed together, little ultimate good will result.

I have pointed out how the Germans, owing to our patent laws, were able to make use of our brains, and one cannot help thinking how fertile those brains were with new ideas, and with initiative to carry out the ideas from the experimental to the manufacturing stage. It must be remembered, however, that the number of these pioneers was not very great, and it is small wonder if, when they found their ideas being exploited by others, they were inclined to lose interest, and retire from the fray. Whether or not this was the case I am unable to say, but in this particular line of industry we seemed to lose our pioneering interest. The existing works in some cases, at any rate, began to live on their past reputation and seemed to make very little effort to compete with their German rivals. On the business side they did not take sufficient trouble to keep their customers or to open out new markets. The dyer was told, if not in words, at any rate by action or want of action, "These colours have always been admired and have been manufactured by us for years, we don't see any reason for altering the shades or the methods of dyeing."

In the meantime, however, the Germans were flooding the markets with new dyes and new shades and sending round their travellers by the score. These travellers were not simply salesmen, but in many cases trained chemists, who were prepared to go into the dyehouse and show the dyer how to apply the dyes.

The question of capital also had a great deal to do with the advancement of the artificial colour industry abroad. In this country all the firms were privately owned, being more or less family concerns. To-day this is in the main still the case. In Germany it was and is otherwise. They are big commercial concerns, supported by outside capital and also by the banks. Furthermore, a large slice of the profits has always been put by for developing the works, for new machinery, and for research work. We in this country have been too prone to take too

much out of the business, instead of building up large reserves. One might say, why then was not outside capital brought in to increase the size and output of the works? The reason probably was this—that capital found a more remunerative opening in shipping industries and the building of docks, the opening up of coal mines, in the heavy chemical trade, and in engineering concerns, etc. Also a large amount of capital was invested abroad to finance British or foreign undertakings from which good profits could be obtained.

One of the chief causes of our not being able to hold the artificial colour industry which had been founded in this country, and the real cause of the German pre-eminence, and for which they deserve every honour, was the lack of industrial research. One of the reasons why so many of the students of Hofmann rose to such eminence was the love of research with which he imbued them. To-day our manufacturers are awakening to the need and value of research, but for many years, although a chemist was attached to most of the works, he had in the main simply routine work to pursue, which either gave him no time or incapacitated him for research, and this is still largely the case. Small wonder is it that our manufacturers were unable to compete with the Germans. In the German works, shortly after their foundation, magnificent laboratories with all the latest scientific apparatus were erected. Libraries stocked with the latest literature were installed—everything was there which might be required for the investigations in hand.

Having made these preparations, chemists were employed who had had a thorough training. Before they could take their degrees it was compulsory that they should carry out an original investigation along some line of research. The engineers employed were also highly trained men with a good chemical knowledge, many of them having received a university education. In the works the chemist and engineer worked hand in hand. Thus, when the chemist had discovered some new material or process in the laboratory, it was further worked out in collaboration with the engineer-chemist. The product first produced in the laboratory was next made on a semi-commercial scale, and if this proved successful, the commercial plant was erected and the material manufactured in bulk.

As the output of the works increased, so the number of chemists taken into the works increased until, as is well known,

some works, such as the Badische, and Meister, Lucius & Brüning, employ over two hundred research chemists. The fact is that almost the whole of the technical staff are more highly trained than is usually the case here. There is also in Germany a much closer relationship between the professors of chemistry in the universities and polytechnic institutes and the manufacturers. This is good for the professors and good for the manufacturers, as it reacts upon the training of the student.

How could British manufacturers who, if they did not scorn research did not recognise its value, compete under these conditions? During the last decade British colour makers have been holding their own in certain lines, and even improving their position, owing to the fact that they have been increasing their technical staff. But they have been, and are, severely handicapped by the enormous German advances and by the great variety of products the Germans have been able to supply to the consumers. The agent of a German firm can go to the dyer and offer him all the shades he requires, the British manufacturer can only supply a few : consequently, the German gets the order—it saves so much trouble.

There are other reasons which are more closely related to the German business methods, but I will not go into these, as I do not wish to enter into controversial matters.

I am not fond of the expression, "War on German Trade." Is it not better to say, "Opportunity for British Trade and the Capture of New Markets"? The Germans thoroughly deserve the pre-eminent position which they have attained in the artificial colour industry. It is in the main due to painstaking research, backed by thorough business organisation. Some of their business methods, it is true, are such that we should not care to see them copied here, but the main reason has been the lack of research, and of making opportunities, instead of waiting for them to come.

Did not the Germans deserve to capture the indigo industry? The research on this subject was carried out on a truly colossal scale. Many chemists were engaged for a period of over twenty years upon research work in order to produce this product synthetically on a commercial scale at a price which would compete with, and even undersell, the natural product. It is stated that before a single pound of synthetic indigo was placed on the market over £1,000,000 had been spent during the twenty years.

The literature, patent and otherwise, upon the subject is one of the finest chapters in the history of chemical technological research. It is not my intention to enter into the details of this magnificent work—time will not permit, and most of you are familiar with it. Had the indigo planters not been so sure of their position, they would—when the first discovery of synthetic indigo was announced in 1878—have carried out experiments to see if they could not improve the quality and quantity of their product, but they sat by with folded hands. When it was too late they cried out that the introduction of synthetic indigo was a bolt from the blue. They should have watched the signs, in which case they would not have been so surprised; aye, they might even have arrested or retarded the falling of the bolt.

I have given some of the chief reasons why the artificial colour industry was lost to this country. There is, however, another one. In the preparation and purification of some of the dyes, it is necessary to employ large quantities of pure alcohol. The enormous cost of pure alcohol in this country, compared to its cost in Germany, owing to Government duty and excise restrictions, has made its use on a large scale prohibitive, and has most certainly been a contributory cause in helping the German manufacturers. Within the last few years these restrictions have been considerably mitigated—largely owing to the persevering efforts of Mr Thomas Tyrer. Unfortunately, much yet remains to be done. Although Government has given relief, the officials who have to administer the Government Acts seem to forget they are public servants, placed there for the good of the country. Several manufacturers to my knowledge, after inquiring into the matter, found the use of alcohol so hedged and bound about with red tape and officialism, that they were unable to take advantage of the Act. In the fine chemical trade, that is the manufacture of drugs and photographic chemicals, the use of pure alcohol is of even greater importance than in the colour industry. The fine chemical trade in synthetic drugs and photographic chemicals never has been a British industry. It is entirely due to German research work, and we have never tried to develop it here. It is, however, a very important industry, and there is no reason why it should not now be developed, at any rate in a partial state, in this country. Alcohol, however, is a very important reagent for this industry. British manufacturers can produce good cheap alcohol, if there is a demand for it; but

while its use is hedged with difficulties, those who use it will employ it in minimum quantities only. Like most commodities, it can be made more cheaply in large than in small quantities.

Let me now briefly summarise the causes which have led or contributed to the present position of the artificial colour industry in this country :

- (1) The character of the British patent laws and the want of patent laws in Germany, whereby the Germans were able to exploit our brains.
- (2) Slackness on the part of the early British manufacturers (after a certain period of prosperity).
- (3) *Industrial chemical research carried out in Germany, but neglected by us.*
- (4) German business organisation.
- (5) Restrictions on the use of alcohol.

That the artificial colour industry is in a bad position is self-evident. A devastating war has broken out, stopping our supply of imported colours, and what is the result? There is a dye famine. Dyers cannot carry out their contracts because, although willing to pay almost any price, they cannot obtain the dyes. It must be remembered also that aniline dyes are used for a great many purposes other than that of dyeing textiles. Paper, leather, bones, feathers, straw, grasses, etc., are all dyed with aniline dyes. They are employed for dyeing wood, particularly in the furniture trade. Very large quantities are used in paints in the form of lakes. Even in confectionary they are employed. All these industries are hit.

So dependent, indeed, are our manufacturers upon dyes, that the stoppage of the supply is beginning to cause great distress amongst thousands of our workers, and this distress will increase as the available supplies are used up. Colonel H. A. Foster recently pointed out, before the Bradford Chamber of Commerce, that although the value of the dyes imported might not exceed £2,000,000 to £3,000,000 per annum, yet taking textiles alone it involves indirectly a turn-over of about £100,000,000. If we take into account some of the other uses which I have mentioned, this enormous sum must be greatly exceeded.

The British colour makers are increasing their output, but since before the war they were supplying only about 15 per cent. of the amount used in the United Kingdom, it is obvious that

they will not be in a position for a long time to meet the demand. Furthermore, the Germans manufactured very large quantities of dyes which have never been made here.

What, then, is to be done? I notice that the Bradford Chamber of Commerce unanimously passed a resolution on 27th October "urging upon His Majesty's Government the vital necessity for immediately adopting measures for furnishing such support as is essential to the establishing and effectual continuance of the manufacture of aniline dyes upon an adequate scale in this country."

To my mind, the most important part of the resolution is contained in the words "and effectual continuance of the manufacture of aniline dyes." If the industry is founded, it is the bounden duty of the Government to see that it is not stifled again at the end of the war.

Capitalists who might be willing to risk their money in putting up colour works say: But what is to happen after the war? The Germans will again flood the market and undercut. In all probability they have accumulated supplies and will be willing to get rid of them at almost any price. Will the Government guarantee that for a certain number of years all dyeing which is done for Government Departments shall be dyed only with British-made dyes? If the Government agree, and the manufacturers and users of this country should compel them to agree, what about other than Government users? Will they rush back to buy in the cheapest market, because it goes without saying that in most cases, for some time at least, the British dyes will not be so cheap as the German, owing to the enormous experience the latter have behind them. On the other hand, in our gas-works we have a great deal of the raw product necessary.

My own feeling is that a large portion of the raw products should be made by some of our large gas-works, that is to say, those which have tar-distilling plants. They have there, in their works, the benzol, toluol, naphthalene, anthracene, etc. With regard to the last-named substance—anthracene—the British Alizarin Company can probably deal with it better than anyone else, but they will require increased supplies.

Why should not nitrobenzene, aniline, nitrotoluene, toluidine, the naphthols, naphthylamines, phthalic anhydride, and many other substances, which are the raw materials for the colour works, be made at the source of supply of the raw products for

their manufacture? About 10,000,000 gallons of benzene are produced annually, and before the war two-thirds of this went to Germany, a portion of which they used for making aniline.

The question is one bristling with difficulties, but it is of instant urgency. Some suggest the establishment of huge works comparable to those of the Badische or Meister, Lucius & Brüning (forgetting that those were built up from comparatively small beginnings), which will manufacture every type of colour and also fine chemicals, a scheme which would mean in the long run a huge financial disaster. Others think that a number of small firms should be founded which would manufacture certain specific ranges of colours. This certainly is more feasible.

My own feeling is that those firms now manufacturing should enlarge their output and obtain leave to work certain German patents; that many of the raw products should be manufactured at one or two of the great gas-works who might, after their plant was working, also make certain dyes and gradually branch out; also that a few new companies with carefully thought-out programmes should be started.

Now in connection with the protection of the industry I wish to say another word. We will presume that the Government will only allow the use of British-made dyes. How about the other consumers? It will be very difficult to bind them. The best solution of the problem would be to give them, or rather get them to take, an interest in the new works, or, for a matter of that, in the old ones. This was done by the Turkey Red Dyers' Association, who, in order to prevent the manufacture of alizarin leaving the country, founded the British Alizarin Company, and agreed to take so much of the output. They were thus not dependent upon the Germans, and also had an interest in the manufacture of the product. Cannot the general dyers do something similar?

In conclusion, I wish to say just one word as to the revocation of German patents. After war was declared, the Home Office revoked all German and Austrian patents, as and during the continuance of the war. It was also stated that in certain cases licences would be granted to British manufacturers to take up and work these patents. I was informed recently by an eminent patent lawyer and by one of the largest patent agents in London, that the granting of licences is practically a dead letter. Further, that where licences have been granted, a royalty is reserved for



the enemy, and there is no certainty that those who have obtained a licence during the war will be allowed to work the patent after the declaration of peace.

If the trade is to come to this country, and to be retained by it, it is of vital importance that these matters be cleared up, and the Government must help.

#### DISCUSSION

The Chairman (Mr E. HICKSON) said many people seemed to think that the colour trade in Germany had been fostered and helped by the Government in a manner which was quite out of proportion with the truth, and those of them who had seen the little jubilee books recently issued by some of the German firms who had celebrated their fiftieth anniversary would know quite well how true was the lecturer's statement that most of these firms started on the most insignificant scale.

The Lord Mayor of Leeds (Mr J. E. BEDFORD) said it was particularly interesting to hear the early history of this subject from the lips of one who bore the honoured name of Perkin. He thought it was their duty to recognise the scientific and business-like manner in which Germany had conducted and developed this important industry. When the present crisis developed, the Government had very promptly set up at the Board of Trade a Chemical Products Committee, and called together eminent business and scientific men to discuss the matter, and see how the stoppage of the textile and printing industries could be avoided. Some of them had taken the view that it would be absolutely necessary, in order to build up and foster this industry, for the Government to give some form of protection. He himself had suggested at a meeting of the Leeds Chamber of Commerce that we should have to put a protective duty of about 25 to 30 per cent. on imported aniline dyes, and his friends had reproached him with the fact that he was a Liberal Free-trader, and was now turning Conservative. He had replied: "I am still a Free-trader, but in extraordinary circumstances and in time of war you must adopt war methods." He believed they had in England a sufficient number of highly trained chemists to develop the industry. He was sure that there were certain of the simple colours which could be tackled at once if the requisite amount of capital were available.

Professor W. M. GARDNER said one point which appeared to him worthy of mention, and which was not included in the list of reasons given for the loss of the industry, was perhaps a fundamental one. Dr Perkin had to some extent touched upon it when he mentioned that in the development of the synthesis of indigo upwards of £1,000,000 had been spent in experiment before any return was obtained. It appeared to him that this would have been quite impossible in England, because the investing public would never have supported an expenditure of any such sum. Want of knowledge and of interest on the part of the investing public had been one not unimportant cause why companies had not been formed for the development of the industry in this country. There were other reasons why it was peculiarly difficult to regain the industry, and here again he should like to touch upon a point which the lecturer, no doubt from lack of time, did not mention ; and that was the important way in which secondary and subsidiary interests had been built round the great coal-tar colour industry of Germany, such as the manufacture of synthetic medicines and synthetic scents and flavourings on the one hand, and the manufacture of necessary reagents, such as fuming sulphuric acid, on the other. These had put the industry in Germany in an extremely strong position, since before we could hope successfully to compete with them we should have to launch out, not only in the manufacture of colours, but in many other directions, so that altogether an enormous outlay of capital would be required. The public must recognise that it was a most complicated question, and one which would require not only great enterprise and co-operation on the part of manufacturers and consumers, but would inevitably require assistance from the Government.

The Lecturer said the subject was so big that he was afraid of digressing on side issues, but he quite agreed with Professor Gardner that one of the reasons why the industry had become so great in Germany was the working up of by-products. What was waste in one product was the starting-point in making another product, and if they were going to manufacture successfully in this country they must pay attention to that fact. It was no use saying they would manufacture this or that dye and neglect all its by-products. If they did, the cost of the dye would be out of all proportion to its cost as it was manufactured abroad.

XXIV.: 1914

## THE SUPPLY OF CHEMICALS TO BRITAIN AND HER DEPENDENCIES

BY SIR WILLIAM A. TILDEN, D.Sc., LL.D., F.R.S.

(*Journal of the Royal Society of Arts*, 27th November 1914, p. 26)

To those who can look back over half a century, the progress of scientific and industrial chemistry, and the relations of the one to the other, present many features of extreme interest. After the days of Lavoisier, and during the earlier part of the nineteenth century, the foundations of theoretical chemistry were laid by the efforts, contemporaneous but independent, of the chemists of England, France, and Sweden. The great names associated with the movement include Davy, Faraday, Dalton, Gay-Lussac, Dumas, and Berzelius. There were no German chemists of the first rank in those days, and if we look among them for fundamental discoveries we can only find one of considerable importance, namely, the discovery of isomorphism by Eilhard Mitscherlich in 1819. But the birth of Justus Liebig at Darmstadt, in 1803, gave to German science a leader whose influence stretches down to our own day, and is felt wherever chemistry is studied or practised. The department of organic chemistry has been the field in which the most remarkable successes have been won, though not wholly, as sometimes represented, by the German chemist.

The relation of optical activity to atomic constitution was the discovery of le Bel, a Frenchman, almost simultaneously with van 't Hoff, a Dutchman, and the application of their theories to the phenomena presented by compounds other than those of carbon was illustrated in the first instance by Smiles, and by Pope and Peachey, all of whom are Englishmen. It will also be only fair to state that while we readily acknowledge with admiration the brilliant work of von Baeyer and Emil Fischer in connection

with the synthesis of indigo, the sugars and the proteins, the fundamental principles which underly all chemical theory have been established almost entirely by the chemists of other nations. It is only necessary to recall such subjects as the atomic theory, the periodic law, Faraday's laws of electrolysis, the theory of free ions, the phenomena of radio-activity, and the discovery of radium, to show that in laying down broad general principles German chemists have not usually been the first in the field, though at later stages they have shown great and commendable activity.

Turning now to the position of industrial chemistry, a single brief quotation from the "Report on Chemical and Pharmaceutical Products and Processes" in the International Exhibition of 1862, from the pen of A. W. Hofmann, then Professor of Chemistry in the Royal College of Chemistry and Royal School of Mines, London, will be sufficient. He says (p. 3): "The contributions of the United Kingdom, and in particular the splendid chemical display in the eastern annexe, prove the British not only to have maintained their pre-eminence among the chemical manufacturers of the world, but to have outdone their own admitted superiority on the corresponding occasion of 1851."

On referring to the table of statistics which appears on the same page of the report, we find that of the 762 exhibitors in the class, the United Kingdom was represented by 200, while Germany, Austria, the Zollverein, and the Hanse towns together mustered only 136. France stood next with 115 exhibitors. It will be remembered that at the date of the exhibition the discovery of the so-called aniline colours was bearing very important industrial fruit. Mauve, or aniline purple, was discovered by W. H. Perkin in 1856, and aniline red was first obtained industrially by Verguin and Renard Frères of Lyons a few years later.

It is also interesting to notice that among the early investigators and patentees of processes connected with the production of colour from coal-tar hydrocarbons, only English and French names are to be found, with the significant exceptions of Hofmann and Caro, both of whom were at that period resident in England. At this time synthetical chemistry in the modern sense was as yet unpractised because unknown. Such an important substance as salicylic acid, for example, was a mere laboratory product, obtainable only from natural sources.

But the activity of the chemical industries in the United

Kingdom is not to be measured only by reference to subjects such as those of the coal-tar colours, nor by the number of exhibitors in an international exhibition even at that early period in the history of exhibitions, at which manufacturers were far more eager to find a place than they have been in more recent times. Statistics in relation to the development of the alkali trade show how rapidly the production of what are called "heavy chemicals" was proceeding at this period. Figures derived from returns collected by Mr Christian Allhusen from 81 per cent. of the manufacturers in the United Kingdom, immediately after the first Great Exhibition, are shown below. These may be compared with statistics prepared by Mr W. Gossage for the year 1861, immediately before the Exhibition of 1862<sup>1</sup> :—

	1852.	1861.
	Tons.	Tons.
Soda ash . . . .	71,193	156,000
Soda crystals . . . .	61,044	104,000
Bicarbonate . . . .	5,762	13,000
Bleaching powder . . . .	13,100	20,000

The value of these products for 1852 was estimated at about  $1\frac{1}{4}$  million pounds, while the value of the products of 1861 was calculated by Mr Gossage at upwards of two millions sterling.

The Board of Trade has recently issued a Bulletin concerning German competition in the United Kingdom market, and on page 2 we find the statement that the soda compounds, excluding chromates and bleaching powder, produced in the United Kingdom in the year 1907, are valued at £3,390,000. The imports from Germany in 1912 are valued at only £8700. As to bleaching materials, the product of the United Kingdom for 1907 is estimated at £527,000, while the import from Germany for 1912 was £44,600.

From these figures the easy deduction is made that "the imports of these chemicals into the United Kingdom from Germany are relatively insignificant when compared with the output of the same articles in this country. It is clear that in these particular lines British manufacturers have no need to fear German competition in the home market."

<sup>1</sup> Gossage's *History of the Soda Manufacture*.

Similar remarks apply to aluminous compounds, coal-tar products not dyes, the cyanides, sulphuric acid, and other acids for which the Bulletin may be consulted. It thus appears that the British manufacturers of sulphuric acid and soda, from the early times of a century ago, have been able, up to the present, to hold their own against foreign competition, and have thus added substantially to the revenues and well-being of their country.

The immense advances in every direction made in all civilised countries have brought demands in steadily increasing quantities for a variety of materials of which many were unknown to the generations immediately preceding our own. These are almost all the outcome of the progress in our own time of chemical knowledge. Since the introduction of the coal-tar dyes the development of chemical theory has rendered possible the production in the laboratory of a large number of organic substances which are either identical with compounds already known as occurring in Nature, or from their ascertained physiological action have added incalculably to the resources of the physician and surgeon in relieving pain and in curing disease. These include not only drugs for internal administration, but antiseptics, the use of which was only beginning to be recognised at the time of the Exhibition in 1862 (*Hofmann's Report*, pp. 104-105).

To these must be added essential oils and other volatile aromatic substances, the application of which to perfumery and flavouring has undergone a stupendous development during the last thirty years.

The innumerable applications of photography have also led to a demand for developing, fixing, and toning materials, as well as for plates and films on a very large scale.

The arts of peace as well as the operations of war have also led to the production of explosives of many new types formerly unknown.

There is also another department of business which requires notice, and that is the demand for pure chemical reagents for analysis and research, which has increased to an extent very difficult to calculate, but is manifestly very large. The modern university and technical colleges, nearly the whole of which have come into existence within the last forty years, the large body of Public Analysts appointed under the Sale of Food and Drugs

Act, 1875, the establishment in nearly all the public schools and high schools of laboratories for teaching chemistry, as well as the numerous technical laboratories connected with such institutions as the Government Laboratory, the National Physical Laboratory, the Metropolitan Water Board, and many others, afford sufficient evidence that there are several hundreds of chemical laboratories distributed over the United Kingdom in which pure chemicals are required for analytical purposes.

Now, leaving to the department of "heavy chemicals" all such things as agricultural and horticultural washes, coarse disinfectants and artificial manures, the question arises: How do we in England stand in regard to the supply of drugs, dyes, photographic chemicals, and perfumes at a time when many of these things are very urgently needed?

It may be safely asserted that the sources of supply of all these materials in the United Kingdom are seriously inadequate. And, further, we may point to the acknowledged fact that many of the dyes, and nearly all the synthetic drugs and photographic materials have been systematically imported from Germany.

The *Annual Statement* of the Board of Trade (p. 108) shows that in 1913 we imported from Germany:—

Alizarin and anthracene dyes . . . . .	£ 271,119
Aniline and naphthalene dyes . . . . .	1,382,478
Synthetic indigo . . . . .	76,681
	<hr/>
	1,730,278

Under the head of "Drugs, unenumerated, including Medicinal Preparations" (p. 107), out of a total of imports from foreign countries and from British possessions amounting to £1,302,860, more than one-fourth, or to the value of £332,464, was in 1913 received from Germany. From this is to be deducted the inconsiderable amount of dyes and other chemicals from coal-tar, valued at £24,691, exported in 1913 to Germany (p. 300). According to the *Final Report on the First Census of Production of the United Kingdom for 1907* (p. 547), this country made 139,000 cwt. of coal-tar dyes, valued at £373,000, of which practically the whole was consumed at home.

As to fine chemicals for analysis and for research, there are no figures available, but it may safely be said that there has been no appreciable production of these things in this country. If

such a statement is met by protests from manufacturers who profess to supply these materials it is only necessary to refer to the experience of analysts and directors of research laboratories, which has compelled many of them to resort habitually to German makers for their supplies of trustworthy reagents.

If we are ever to be in a position to supply ourselves and our dependencies with the dyes, the drugs, and the rest of the fine chemicals required in our work, it will only be achieved after a careful review of the circumstances which led to the removal of the industries from this, the country in which many of them originated, together with a determination to take to heart the lessons of the past.

A chemical manufacturer, discussing the neglect of fine chemicals in this country, recently made the remark: "What does it matter, if we are making money?" I venture to say that that view expresses neither patriotism nor common sense. For the same principles which have served as the basis of the German success in relation to dyes and fine chemicals apply equally to the production of heavy chemicals, and already German chemists have been boasting that, having secured the trade in the former, they are about to attack the latter.

The export trade in sulphuric acid alone is already three times as great from Germany (1912) as from the United Kingdom (1913), as shown by the figures given in the recent Bulletin issued by the Board of Trade (Commercial Intelligence Branch, October 1914).

The recent success of Professor Haber, of Karlsruhe, in the synthetical production of ammonia from hydrogen and atmospheric nitrogen, a process which has been put into operation on an industrial scale by the Badische Company, ought surely to carry something significant to the unprejudiced mind. Neither is it superfluous to point to the extensions taking place in several countries of operations in which the nitrogen of the atmosphere is being fixed in the form of cyanamide, of nitrites and nitrates in which the industrial lead has been taken by Germany, which also supplies a large proportion of the capital, though at present not to the exclusion of the British.

The extent to which the German chemist arrogates to himself the whole field of scientific and industrial chemistry is illustrated in the report (given in full of *Nature*, lxxxv. p. 558) of a lecture given by Professor Emil Fischer on 11th January 1911, in the



presence of the Emperor, on the occasion of the inauguration of the Kaiser Wilhelm Gesellschaft zur Förderung der Wissenschaften. It is at least unpleasant to hear of a man so eminent as Professor Fischer, and so worthy of respect, treating the subjects of his discourse as though every one of them had originated and been developed in Germany. Perkin is indeed referred to as the discoverer of mauve, but every other foreign name is omitted.

If I now try to recall some of the circumstances which led to the gradual transference of the colour industry from this country to Germany, and the failure to establish here any appreciable production of the synthetical drugs and other chemicals now so urgently needed, it will not be the first time the facts have been stated and the obvious conclusions deduced therefrom.

All the substances referred to belong to the department of organic chemistry, and it might perhaps be supposed that neglect of this branch of the science by the chemists of this country was the cause of the loss of business. When Hofmann was unfortunately allowed to leave the College of Chemistry to return to his own country, a check was for some time observable in the output of research among us, but it must be remembered that the number of institutions in all countries in which the study of chemistry was pursued was then relatively small. Even in Germany the Chemical Society in Berlin did not come into existence till 1867, and up to that time there had been no laboratory for practical instruction in chemistry in the university of that city.

For the last thirty years, however, the progress of research in this country has gone forward at an increasing rate, though still less rapidly than in Germany. The slow development of chemical teaching and research in this country was attributed by many people to the anti-scientific influences at work in our universities, and especially the older universities. This point of view was exposed very clearly and forcibly by the late Sir William Perkin in presidential addresses delivered to the Chemical Society and the Society of Chemical Industry in 1885 (see p. 75, *ante*). And up to this time it would be indeed difficult to exonerate Oxford and Cambridge from responsibility in the evil example shown by those great seats of learning. But since that day many changes have taken place, and great advances

have been made. What is wanted in the British universities is, first of all, that no man shall in future be appointed to a professorship, or indeed to any teaching post in connection with physical or natural science, who does not show his ability to instruct in the higher branches of his subject by the character of the researches which he continues to carry out during his tenure of office ; and, secondly, such a change in the curriculum and endowments that there may be not only a supply of instruments and materials but a sufficient body of trained assistants in the form of advanced students to enable the professor to pursue without delay any promising line of investigation.

Notwithstanding the difficulties which stand in the way the scientific chemists of this country are, however, not idle. Evidence of this may be seen in the *Transactions of the Chemical Society*, the volume of which for 1913 contains 238 papers extending over more than 2300 pages. And when it is remembered that these papers have survived the severe censorship exercised by the Publication Committee of the Society the result must be considered encouraging. It appears, then, that it is not to the scientific part of the chemical world that blame attaches in recent times.

Forty years ago it would be safe to say that there were practically no chemists engaged in the direction of the chemical works of this country, and by chemists I mean fully qualified scientific men. Probably in the palmy days of colour-making it would have been difficult to meet with a British manufacturer who had ever heard of Kekulé's benzene theory, or would have thought it worthy of a moment's notice by a practical man. And yet at the Kekulé Jubilee in 1890 a representative of the German coal-tar colour industry declared that the prosperity of Germany in this direction was primarily due to this theoretical conception. Even in much later times the chemical manufacturer in this country has repeatedly had facts laid before him which ought to have attracted his serious attention. One of the most convincing statements was laid before this Society by Professor Meldola on 13th May 1886 (see p. 121, *ante*), and one would suppose that the figures then given would have been sufficient to create well-founded alarm. For he showed, on the testimony of a considerable number of prominent English dyers, that already about nine-tenths of the colours employed by them were

imported from Germany. Again, in a lecture given before the British Association in 1901, on the "Relative Progress of the Coal-tar Industry in England and Germany during the Past Fifteen Years" (see p. 189, *ante*), Professor Green showed clearly the steady increase in the imports of dyestuffs from Germany into England, and the steady decline in the production of similar materials in England.

Finally, we have the fact known to all the world that one of the most notable triumphs of German chemical industry is the production of synthetic indigo made from naphthalene on a scale so large as to have almost driven the Indian planter from the field. In this case we have over again a story nearly corresponding to the history of the introduction of artificial alizarin in 1869, an event which was speedily followed by the abandonment of the cultivation of madder in the south of France and elsewhere. And to-day we learn from the Board of Trade Statement for 1913 that we imported indigo from Germany to the value of £76,681, while the value of the natural indigo from India has declined from £124,112 in 1909 to £48,208 in 1913. As to the cause of this serious reduction of chemical business authorities are unanimous.

Perkin, in the address to the Chemical Society already quoted, attributed the success of the German industries to the employment of high-class chemists (*Trans. Chem. Soc.*, xlv. [1884], p. 219 *et seq.*).

The same view was expressed by Professor Meldola in his paper before this Society in 1886. "The strength of our competitors," he says, "is in their laboratories and not, as here, on the exchanges."

Professor Green stated as his opinion, in the lecture referred to, that the remedy for the present state of affairs can only be found in a better appreciation of the value of science throughout the length and breadth of the land, and that it is not so much the education of our chemists which is at fault as the scientific education of the public as a whole. Nor can much improvement be expected till the public, including manufacturers, can be disabused of the fallacy that a year or two of technical training pumped into an ignorant schoolboy will produce a better works chemist than a university course of scientific study laid upon the foundation of a good general education.

If these are supposed to be merely the prejudiced opinions

of British chemists, the sentiments expressed by German manufacturers themselves may be appealed to.

In 1900 a lecture was delivered on the occasion of the opening of the Hofmann House in Berlin by Dr H. Brunck, since 1884 chief technical director of the Badische Company, on the "History of the Development of the Manufacture of Indigo" (see p. 204, *ante*). This lecture, in the form of the English version issued by Dr Brunck, may be fairly regarded as a sermon preached to British manufacturers. Its perusal will convince anyone that the success which has been achieved is the reward of long-sustained investigation in the laboratory of the scientific chemist, and to do justice to this conviction I wish every chemical employer in this country could be induced to read the weighty and eloquent words of the author. He would then perceive that to permanent industrial success there is only one road, and that the way pointed by science.

I will content myself with quoting only a passage or two from Brunck's lecture :—

"With grateful admiration and reverence do we recall those ever memorable masters, Kekulé and A. W. von Hofmann, whose gifted achievements have laid the foundations of our industry. And when we look back at all the technical achievements we also gratefully recall the fertile discoveries of Graebe and Liebermann, of Peter Griess, and the beautiful researches of Emil and Otto Fischer, of O. N. Witt, and the numerous other investigations conducted in our university laboratories, which have acted as incentives for chemical industry, and have furnished the foundation for renewed progress. But first and foremost we are impressed by the mighty influence of the investigations of A. von Baeyer, to whom the coal-tar colour industry is indebted for a great number of important achievements, and who himself has, to-day, unfurled before you the picture of a magnificent scientific creation, from which it was possible for chemical industry to construct and develop one of its grandest achievements.

"But this infant industry was no longer content to be dependent on the gifts which were made to it from various scientific sources. Renowned investigators placed themselves entirely at the disposal of chemical industry; young men in great numbers devoted themselves to it, and grew up with it in enthusiastic and self-directed activity. Such men as Caro,

Glaser, Martius, and later on Laubenheimer, Duisberg, Bernthsen, and many others, introduced the spirit of scientific investigation into industrial practice." And, in conclusion, he says: "You have seen that this new industry is not an unexpected gift fallen from the heavens, but that in order to complete the task the intellectual labour and the industry of many men had to be co-ordinated in an organised attempt to attain a definite object for a number of years and throughout a considerable period when success could by no means be regarded as certain. The pre-requisites for practical indigo synthesis were supplied by the results of long years of scientific labour."

In the semi-annual report for April 1903 issued by Schimmel & Co., the famous manufacturers of essential oils, there are some figures which show the increase of chemical works in Germany and the great increase in the numbers of qualified workmen employed therein, on which the firm makes the following remark:—"The foregoing figures show clearly that the German chemical industry has passed intact through the economic crisis of the last few years. Further, there are no grounds for fearing that it will be outstripped by competition from abroad, so long as the German universities possess such eminent representatives of chemical science."

It is now time to consider what ought to be done and what it is possible to do in this country to remove reproach from British chemical industry, and to render the Empire independent of supplies from foreign sources.

We need many first-rate chemists, a few engineers, plenty of capital, and some good men of business. A combination of these elements in due proportion is certain of success, and the time, though so unhappy for the world, is favourable for this enterprise.

Inasmuch as the functions of each and the best way of combining them have already been settled in practice on the Continent, it is to be hoped that the ancient precept about being taught by the enemy—*fas est et eb hoste doceri*—will not be forgotten. For there can be no doubt that the principle acted on in all German chemical factories, namely, the employment of the best available scientific skill and the constant appeal to scientific research, has been the secret of their success.

In the British colleges and universities there are many able young chemists, but many more are required. Here education and industry interact on each other. If the demand for scientific

assistance were more general, the supply of well-qualified men would soon be greatly increased, and greater attention given by the teachers to the industrial side of the subject. At present other professions in which the prospects are more alluring attract into other lines of work much of the talent of the country. This, however, is not to be interpreted as meaning that there is not now a supply of able young chemists sufficient for immediate needs. The difficulty is to induce chemical manufacturers to treat them reasonably. The pay offered is generally insufficient, and though conditions are somewhat improved of late years, the employer too often expects immediate profitable returns from the engagement of a scientific man. In the Badische works at Ludwigshafen the plan has been to engage university men on the recommendation of their professors for a term of years, at a salary which will enable the new members of the staff to live at least modestly. I am told that in some American works the same system has been adopted. These young men are placed in the research laboratory under the chief chemist controlling the department of manufacture selected, and it is not expected that they will accomplish anything very remunerative at first. But their future depends on their ability and activity, and they act accordingly.

Then there is the position to be accorded to the engineer. He is, of course, indispensable; but the part he should play in the works depends on the nature of the processes involved. So far as relates to buildings and other structures, to supplies of water, fuel, power, and electricity, the engineer has the field to himself, but the operations in which materials are to be employed in producing and controlling chemical reactions which lead to the desired product belong to the chemist, and here he ought to be supreme. In some of the old-established operations an engineer with an elementary knowledge of chemistry may carry on for a time, but in these days a chemist with the most extensive and intimate knowledge of physical chemistry is necessary if these processes are to continue to be profitable. As to the production of dyes and other organic synthetical products, the operations involved are in many cases so nearly similar to laboratory processes that the chemist requires very little assistance from the engineer.

As to capital, it is necessary to remember that it will have to be provided liberally. A single fact mentioned in Brunck's

lecture on indigo, given already fourteen years ago, shows the spirit in which the German manufacturers attacked the problem of the industrial production of this one colouring matter. They had then invested about £900,000 for this purpose.

The works of the Badische Anilin- u. Soda-Fabrik at Ludwigshafen are arranged on a plan, which clearly recognises the inseparability of research and manufacture. A number of rectangular buildings, four storeys high, are so arranged that the railway lines may traverse the works in two directions at right angles to each other. Each building is devoted to the production of one substance or closely allied group of substances. The top floor is occupied by the laboratory of the chief chemist attached to that department, with several assistants. Below is found an intermediate floor where processes previously tested in the laboratory, or suggested as the result of research, may be tried on a scale sufficiently large to determine their practicability before being transferred to the lower floors where the actual manufacture is conducted. I doubt if anything so complete or so commercially successful exists elsewhere in the world.

How many chemical manufacturers among us can boast that they regard science in a light so serious as to have provided in their works a properly equipped laboratory with a competent staff whose occupation is not confined to the analytical testing of materials or products, but extends to the systematic endeavour to introduce improvements into old methods or the discovery of new ones? A few such enlightened firms do exist, but the figures quoted show how much mischief has already been done.

A variety of other questions have recently been raised in view of the circumstances which have been forced on our notice by the war. There is not time for the discussion of the state of the law as to patents, but a couple of sentences in Schimmel's report for April 1908 show that "great alarm has been caused in the wholesale chemical industry of Germany by the new British Patent Act, which came into force on 1st January 1908, according to which every patent may be declared void if it is exclusively exercised abroad without sufficient grounds. Many firms are thereby compelled to transfer a part of their production to the United Kingdom, a fact which, in the interests of many thousands of German workmen, is sincerely to be regretted."

With regard to duty-free alcohol, I am informed, on the best

authority, that the regulations in this country are now comparable with those of the German Government, and that there is very little ground for complaint. In the vast majority of cases suitably denatured alcohol can be employed without loss or inconvenience.

There has been a good deal of discussion on the subject of trade-marks and proprietary names, much of which I regard as futile. With regard to drugs, there should be no great difficulty in instructing the medical profession in those comparatively few cases in which the names are changed.

In conclusion, two remarks only require to be made. The establishment of what will be practically a new industry in this country will require consideration and assistance from the State, if it is to survive the period of fierce competition which will follow the conclusion of the war. Encouragement is already promised to the dye industry, in the form of definite financial aid to be given by Government. But remembering that the colour-maker is dependent on the production of many chemicals, which represent intermediate stages in the processes which lead from the raw materials to the finished product, and that the production of these chemicals is naturally associated with other chemical manufactures, it is to be hoped that the temporary production will be extended beyond the immediate field of the colour-maker.

The other remark may raise a smile on the part of those business men who are moved only by commercial considerations. There will be a great temptation when the war is over to resume former business relations with the enemy. The German chemical manufacturers have a powerful organisation and many years of experience behind them. Let them keep any markets they can retain outside the British Empire, but every man who cares for his country will surely demand that business at home shall be limited to British goods.

#### DISCUSSION

The Chairman (Sir WILLIAM RAMSAY), in opening the discussion, said the paper emphasised what we had been told so often during past years, that too little attention had been paid to the scientific side of chemical manufacture in Great Britain. But there were two aspects of the question which had not, he



thought, been sufficiently touched on. The first aspect was as follows: Trade was regarded in Germany as a war; all means of conquest were looked on as permissible. At the annual meeting of the Society of Chemical Industry in 1903, he had said: "It was the Prussians who first showed how a modern army should be organised . . . they have at Berlin a council which arranges each particular of each possible campaign; the men are known who will take the command, and from rank to rank the knowledge is spread as to what particular part each officer and each man will have to play in the campaign. The matter is not left to chance. . . . An exactly similar policy is being pursued by Germany in the matter of industry. It would be curious if it had not occurred to the persons who are responsible for the military organisation of Prussia that a similar policy is applicable to commerce. It would be remarkable if, having succeeded so well in their military organisation, no attempt had been made to establish a similar commercial organisation; and we shall not go wrong if we assume that there is a council whose proceedings are kept quiet but which takes into consideration the statistics obtainable, and as far as possible legislates, or endeavours to legislate, on the basis of these statistics. Where fiscal duties are found to be wanted, such a council puts them on; where there is an advantage in taking them off, they take them off. Where cheap transit is possible, they let it be given; for the railways are the property of the State. Is it to be expected that any country can fight such a combination as that without adopting, at all events, something of their methods, or without studying their methods, and without combining together, if not to imitate them, at all events to thwart them?" He had put the second aspect of the case in a leader in *Nature*, on 12th November 1914. He would quote it. Dealing with the organisation of a German chemical business, he pointed out: "First, the management consists, not in a board of well-meaning elderly gentlemen with a works-manager in their employment, but in a board of specialists, whose business in life is to manage the factory financially, chemically, and as engineers, and who are very highly paid for their services. Second, these gentlemen and a special staff are continuously on the look-out for any scientific discovery or invention which can prove of advantage to their business. Third, a very large staff of men, trained in universities or technical schools, is turned on to the problem of making such a discovery

commercial, whether by securing cheap raw material, cheapening the process of manufacture, or creating a public demand for the article to be manufactured. Fourth, a legal staff is maintained, whose business it is to protect by patent all improvements, however apparently trivial, and to describe them so vaguely as to conceal them from their competitors; these gentlemen, in some cases, have also to advise whether piracy is likely to be successful: whether it may not be possible, by infringing a patent, so to saddle an opponent with legal expenses as to break his competition. Fifth, such companies are so powerful that they can influence the central Government to protect all new developments, whether by imposing duties on articles which might possibly compete, by extending bounties to exported products, or by securing advantages in freights to the coast, and in shipping the goods abroad. Sixth, agencies are maintained all over the world whereby the article is introduced to the notice of foreign purchasers; and last, an extensive credit system is encouraged." German competition was thoroughly organised and systematic; their plan had been to attack some material manufactured here, and, by one of the means alluded to, to render its manufacture unprofitable. Having obtained a monopoly, prices were raised. That was a not unusual method of commercial warfare; but it was only in Germany that all the resources of the State were combined to render it easy. How were such tactics to be met? First of all, there must be co-operation and trust among our chemical manufacturers. They had to be taught to fight, not each for his own hand, but against a common enemy. Smaller works, which had not funds to maintain an expensive research staff, must combine to obtain efficient laboratories. The products of one works must supplement those of another, and the manufacturers must be organised. Second, competition which was unfavourable, owing to fiscal regulations or patent laws, must be combated by the action of the State, after advice and careful consideration, so that our manufactures and trade might not be unfairly attacked by duties, by export bounties, or by easy freights.

Professor JAMES J. DOBBIE thought it might confidently be said, with regard to the supply of trained chemists, that at present this country was in a better position than ever it had been before. In the smallest of the Scottish universities, owing in the first place to the munificence of a former professor, and more recently

owing to the operation of the Carnegie benefaction, a research laboratory had been founded and endowed, which was now well able to hold its own with any laboratory in this country, and with many of the German laboratories. At present there were no less than twelve students there, all of whom were in a position to take part in work to which they had been invited by a committee of the Royal Society, namely, assisting in the production of certain drugs which were necessary for the Army and Navy, and which at present could not be had from the ordinary sources of supply. He thought that was an encouraging circumstance. As to the capital, no one would doubt that that would be forthcoming if it were to be employed for the particular purposes of developing the chemical industries which had hitherto been in the hands of the Germans. But there remained the further point: Were the chemical manufacturers themselves ready to employ the scientific assistance which was needed, and were they ready to remunerate it adequately? Unless they recognised the necessity for the employment of the highest science in the development of their industries very little progress could be made. It was to the education of the masters of the industry that attention had to be devoted. He was glad the author had called attention to the fact that this country had contributed some of the great fundamental principles to chemistry. There was no want of originality in this country; there was no want of initiative; where we had got behind was simply in the power of organisation, or rather the failure to organise.

Mr A. E. BERRY said that manufacturers had not always received the assistance and help which, in his opinion, should have been afforded to them. A few days ago one of the companies in which he was interested received an inquiry for a certain product that had always been made in Germany. That product required pure duty-free spirit. His company wrote to the Inland Revenue, saying they had accepted the business and must have duty-free spirit. That day he had received a visit from an officer of that department, who had spent an hour and a half arguing that the product must be made by something else than duty-free spirit. He claimed that manufacturers in this country had the knowledge and scientific ability to manufacture such a product, but were debarred from doing so by the Government restrictions with regard to duty-free spirit.

Professor A. G. GREEN remarked that the question, as the

author stated, was simply one of knowledge. The Germans had considered it was worth their while to pay in order to obtain knowledge ; we had not, and until we had changed our methods we should still continue in the same old way. An instance had come under his notice a few days previously which showed the manner in which we were accustomed to proceed in this country. A certain firm in the North of England, of very considerable standing, had their attention directed to a certain substance, and were advised it would be a very profitable thing to take up. Instead of making inquiries as to where they would obtain the best scientific skill and advice as to the manufacture of it, or instead of engaging a chemist, they advertised for a workman who had made the product. They succeeded in getting a workman, and the man then immediately said he must have a certain raw material. It was not to be obtained. Then they had to consider the question of manufacturing the raw material. They then proceeded to advertise for another workman with a knowledge of its manufacture. He (the speaker) did not know the sequel, but he thought it was pretty clear what it would be. Sir William Tilden considered there were no difficulties with regard to industrial alcohol at the present time. He (the speaker) was of that opinion until a month or two ago, but from inquiries he had made he was no longer of that opinion. The law as it stood would, he thought, if interpreted in a liberal manner, suffice to give all that was required, but as the law was now interpreted it did not. For instance, the price of ether in England was nearly three times as much as it was in Germany. That simply excluded the manufacture in England of a large number of materials in which ether was required. The Excise authorities absolutely refused to allow ether to be made from pure alcohol ; it had to be made from industrial alcohol. That put a large extra cost on the manufacture of ether from several points of view. Acetic ether was another product which was debarred from being made from pure alcohol, because the Revenue people considered it would be possible to regenerate alcohol from the acetic ether ! Ether was the starting-point of the manufacture of quite a number of fast yellow dyestuffs, which it was impossible to make in this country owing to the fact he had just stated. But he did not mean to say that the alcohol question was one of premier importance. The question of the employment of chemists came first. The British manufacturer must employ a larger number

of chemists, and he must reward those chemists sufficiently to make it worth their while to do their utmost.

Mr A. CHASTON CHAPMAN said that there was a very large body of British manufacturers who imagined that the office was the central and most important part of their works, and that all they had to do was, that if they paid their chemists (if they employed scientific assistance at all) £100 per annum, to ensure that at the end of the year there was £150 in their till. It seemed to him that not only that section of the British manufacturers had to be educated, but also the British public, who in such matters were exceedingly ignorant; and it was through the British public that pressure could be brought to bear on the authorities—where pressure was very badly needed.

Mr WALTER F. REID remarked that he did not grudge the Germans the slightest bit of profit they made out of their own inventions, but when an invention was made in this country and it had to go abroad to be worked, there was something radically wrong in the way the British inventor was treated. He could give dozens of instances where inventors had produced good ideas, but, owing to lack of help and opportunity, had had to let their ideas die or sell them for a mere song. That was not a healthy state of things. He might mention that he invented smokeless powder. In the first place he had taken it to a Government factory, and explained its properties. Some time after an official waited upon him and said that all he claimed for the powder had been proved, but that it could not be introduced into the Army because, if it was, all the rifles would have to be altered!

The Government should assist inventors. British manufacturers were in the position of an untrained mob going against a drilled army. The commercial aspect of the matter was, in his opinion, of the greatest importance, but the author in his paper had put the business man last. He (the speaker) ventured to suggest that some of the largest and best industries in the country had been developed in the first instance by good men of business.

Colonel CHARLES E. CASSAL (President of the Institution of Chemical Technologists) said plenty of trained scientific chemists were certainly necessary, but it was forgotten that in order to produce the trained scientific chemist a long period of technical education was necessary, which put a very severe tax upon the

father of the young chemist. After that, he had to be offered something which was worth his while, and which would attract the right sort of man. Many manufacturers in this country had followed the objectionable practice of appointing Germans as their chemists in preference to Englishmen, because the former were "cheaper." He hoped that an end would be put to this.

XXV.: 1914

## BRITAIN AND GERMANY IN RELATION TO THE CHEMICAL TRADE

BY WILLIAM R. ORMANDY, D.Sc., F.C.A.

(*Journal of the Royal Society of Arts*, 4th December 1914, p. 46)

THE fact that Germany has slowly but surely been gaining control of the greater part of the chemical industries of the world has been brought home to this country times innumerable during the last forty years. It is true that this control has not extended to the manufacture of what are known as heavy chemicals, where questions as to the cost of raw materials, fuel, and freight are of deciding importance. The present unhappy state of Europe, causing a shortage of many drugs and chemicals, has brought this control home in an unmistakable way to the public, who have been made to realise what the manufacturers have known and ignored for at least a generation.

It is probable that the laws relating to the influence of environment, which have been proved to be so important in the animal and vegetable world, will be equally applicable to the development of industries, save that influences, such as national temperament, education, and financial relations of a complex nature, have to be brought into consideration. Industrial development on a very large scale was first rendered possible by the introduction of the steam-engine as a power generator and the provision of adequate means of transport. At a period during which this development was taking place here, the rest of Europe was in a sufficiently unsettled state to permit of this country, without serious opposition, becoming the workshop of the world. No finesse was required to sell the output of our mills and our ironworks. America, like a healthy growing child,

had an inconceivable appetite for all those finished and intermediate products which could only be produced by a nation whose industries had been slowly developed and well established. In those days the English manufacturers, who paid low wages and exacted long hours, made enormous profits. The experimenting which had to be done to develop the various industries was of a rule-of-thumb character and essentially non-scientific in its nature. Probably no nation is so well fitted as the Anglo-Saxon race to develop rapidly along such lines. As a race our people are practically inclined, and so long as development required nothing more than the close application of a healthy common sense, progress was astonishingly rapid. A very old man, whose family was one of the earliest to take up the manufacture of cast steel in this country, has told me that in the early days of the firm's history it was no uncommon thing to receive orders for tons of steel required for the manufacture of drills and tools to open up the virgin wealth of America, in which not only was no price mentioned, but it was explicitly stated that within the bounds of reason quick delivery would compensate for any price. The products of our boiler yards were famed throughout the world, and incredible profits were made by firms whose successors have found the competition of recent years more than they could support. This was, of course, due to the fact that in the days of prosperity the profits were divided to the last penny, the machinery was allowed to get out of date, and the working people refused any longer to play the part assigned to them by the manufacturer in his profit-making schemes. Dr Mollwo Perkin has probably given the correct explanation for this pronounced tendency of British manufacturers to starve and bleed their own business. The rapid industrial development of foreign countries called for enormous capital for railways, shipping, docks, and harbours, and the opening up of mining and agricultural properties, and it was felt that a better return could be obtained from such ventures. English spinners and weavers were supplying the whole world with their products, while loom and mule machinery makers were working day and night to supply these foreign purchasers with the machinery for their infant industries which were in future years to compete with the home country for their own and neutral markets. For close upon a hundred years the tide flowed in our favour. There was no necessity to practise economy.



Nature had been lavish with our raw materials, our insular position and the proximity of our manufacturing centres to the sea-board gave us natural advantages which, added to a favourable situation in international relations, rendered the growth of our material success inevitable. To the thinking mind, it was obvious that such a concatenation of favourable circumstances could not continue indefinitely. We provided other countries, at great profit to ourselves, with all the means necessary for competing with us in these markets in which we had hitherto enjoyed a practical monopoly. Our own works were frequently equipped with out-of-date machinery, which was busily employed in making more modern plant which was put into the hands of those who realised that they would have to exert their powers to the utmost if they were to gain a fair share in the barter of the great international bazaar. The British industry of to-day is in the position of a son inheriting an established business, and having in addition a very large income derived from the labours of past generations. Properly used, such a situation should make for enhanced prosperity; but even such powerful advantages may be nullified if the effort to work along the lines which proved successful in our grandfathers' days be continued too long. Capital directed by ignorance and apathy cannot hope to compete for ever against the forces which are brought to bear to-day.

The industrial life of Germany may be said to have commenced little more than a generation ago. To all intents and purposes an inland country, with little sea-board, they were under a huge disadvantage in every department which required raw materials obtained from abroad. In many directions their natural resources were comparatively poor. They had no iron ores which were comparable with the hematites of Cumberland, their limestone was largely dolomitic, their coals were for the most part poor in quality, and lay often in distorted seams, more like those of our Bristol coalfields than the comparatively easily worked deposits in our northern area. It was recognised at an early period in their industrial development that national progress in a country situated as was their own could not be left entirely to individualistic effort. Nationalisation of railways and canals became an obvious necessity if differential traffic rates were to be allowed, and differential rates were an absolute necessity if large industries were to be developed in the interior of Germany

far from the sea-board. Too much credit cannot be given to the far-sighted way in which every problem of agriculture and industry in Germany is regarded from a national standpoint. It is realised by everyone that individuality must be, to a certain extent, fettered for the benefit of the nation as a whole. In this country individuality runs rampant, and except in times of stress, such as those through which we are passing, the national or Imperial bearing of any individualistic action receives not the slightest consideration. The very people whose fathers sold land to the railway companies at absurdly inflated prices now complain that, owing to the high railway freights in this country, they cannot make adequate profits from the investment of the money obtained from those same companies by an earlier extortion. No doubt many of those who have made their profits from such action would like to see the English railways nationalised and freights reduced at the expense of that patient beast of burden, the British public. Whereas Germany is continuously developing her network of waterways, we in this country, with a customary lack of national forethought, allowed our waterways to become controlled by the railway companies.

Having thus settled the enormously important question of transport, Germany had to consider the lines along which she should seek for an expression of her industrial destiny. Agriculture, there as here the largest individual industry, received attention which is as striking as is the lack of it in this country. Proper afforestation schemes were rendered compulsory; enormous areas of land fit for little else were put under potato cultivation, and science was called in to help to create a new outlet for the crops. Germany became essentially the starch-, glucose-, and alcohol-producing country of Europe. Other large areas were used for the cultivation of the beet, and once again science was called in to assist in the disposal of the roots as raw materials for the production of sugar. If the manufacturing of iron had to become a great industry, it was necessary to develop economic methods for the utilisation of the great deposits of low-grade phosphatic iron ores which were those chiefly available. In addition to the home deposits of iron ore large amounts have been imported, but how successfully the problem has been tackled is shown when we consider that twenty years ago the German production of iron was a mere fraction of our own, whereas to-day the German output exceeds

the British by nearly 100 per cent. The problem of working up the complex metallic ores has fallen almost entirely into German hands. They alone were willing to spend the time and money necessary on researches pertaining thereto, and they alone seemed willing to devote that close chemical skill and attention which is necessary in dealing with these complex problems. In the early days of the chemical industry it must have been quite evident that Germany could not hope to compete in those branches of heavy chemicals such as soda ash, caustic soda, sulphuric acid, bichromate of soda, alum, etc., where cheap raw materials, freights, and cheap fuel play a greater rôle than chemical skill and complex machinery. There is, however, not the slightest doubt that Germany realised years ago what this country has not yet grasped—namely, that all industrial development tends to become more and more scientific. The adequate utilisation of the by-products from an industry may settle the question of the survival of the industry itself.

The necessity for broad co-operation in great industrial problems was recognised and acted upon in Germany in a hundred directions. By-product recovery coke ovens were installed in the immediate neighbourhood of the blast furnaces, and the surplus gas from both was used for power generation. The steelworks were erected in the immediate vicinity of the blast furnaces, so that the surplus power might have an economic outlet. Where it was impossible to bring the steelworks to the vicinity of the coke ovens and the blast furnaces, the surplus energy from these was transmitted far and wide in the form of high-tension electric current sold at an astonishingly low price and thus tempting to the introduction of new small industries within the immediate area. The by-product recovery coke ovens were required to another end. Slowly but surely Germany had been developing her fine chemical industries, drugs, and dyes. Many of these manufactures were dependent for their raw materials on products only obtainable in quantity from this country. We have been building up an enormous industry, not only in the spinning and weaving of cotton and woollen yarns and fabrics, but a correspondingly great industry in the bleaching, dyeing, and finishing of these products. This has been chiefly developed on dyes obtained from Germany, but while we have been content to leave ourselves entirely in the hands of others, the Germans have, by the exercise of

scientific skill and a sensible use of capital, rendered themselves independent of this country. German capital was spent like water to foster the development of by-product coke ovens and in the development of the allied fireclay trade for the production of suitable apparatus, to the end that fifteen years ago practically the whole of the hard coke produced in that country was made to give up its toll of by-products which were the raw materials for their great chemical industry.

At a recent meeting of the Society of Chemical Industry, Professor Henderson referred to the chemical industries of Germany as being merely the development of the crumbs from the British loaf with which they had had to content themselves. In so far as the metallurgical industries are of necessity chemical industries, the term "crumb," as applied to an iron and steel trade much greater than our own, seems out of place, and the remark is only another unfortunate example of the willingness that exists in many quarters to pander to an already too strongly developed feeling of national self-esteem. The British as a nation never show up so favourably as when they are placed face to face with difficulty. As a race we have so much of which we can be genuinely proud that it is a little less than treason when those to whom the people should look for guidance and warning feed them with fulsome flattery and lull them to continued sleep with mental opiates. In ever-increasing degree, both in this country and Germany, the population are dependent on industries for their livelihood. Both countries have long passed the stage at which their home market is capable of keeping the industrial machine in full activity. In addition to each being the other's largest customer, both have to look to the rest of the developed parts of the world for an additional outlet. Someone has said that a nation gets the newspapers it deserves. Judging by what has appeared in some portions of the daily Press during recent months upon the subject of German trade, it is devoutly to be hoped that the common sense of the British nation will not be judged thereby. During the past ten years a nation of over sixty millions has been increasingly occupied in industrial operations. Our own smaller population has, on the whole, been equally fully employed during the same period, and yet people write as though there was a possibility that a large proportion of the activities of the larger nation could be profitably undertaken in the smaller country whose work-people have been for the most

part well and profitably employed for the last decade. The absurdity of this requires no refutation. Indignation is expressed at the discovery that German people and German capital are by way of controlling an ever-growing number of industries in this country. I have not seen that any serious attempt has been made to the much more serious end of discovering why the Germans should desire or should be able to get such a foothold in this country. In some few instances I could supply an answer from my own experience. We have already seen how the German Government brings science and agriculture to work together in afforestation, and the cultivation and utilisation of potatoes and beetroots, but throughout the German national history the Government has recognised that, as a people, they are in ever-growing degree forced to live on industry, and that modern industry is built on the hand-in-hand co-operation of science and capital. This country is dependent upon industrial development for its very existence in a higher degree than Germany, and yet so far as governmental assistance or interest is concerned the principal occupation of the British people might be the signing of dividend coupons. The German Government is incomparably poorer than our own, and yet the financial assistance which it renders to technical education is immeasurably greater. The standard of general education is undoubtedly higher, no doubt largely in consequence of the temptation offered by their one-year service system in the army to those who have passed a certain high standard of efficiency. In a land where the standard of payments is, on the whole, much lower than our own, the leading men of German technical schools are far better paid than in this country. The heads of the technical school staffs are encouraged to become acquainted with the latest technical progress. It is fully realised that a purely academic teacher cannot turn out first-class technical men. The technical industries instantly claim, at higher salary, the members of the staff of technical colleges who have carried out original investigations which seem likely to open out industrial possibilities, and it is not an uncommon thing for such a man to be reclaimed by some technical institution at a later date at a still higher salary. It is realised that the right man, who has work experience as well as technical knowledge, is worth far more to the nation as a teacher than in a private capacity. If an industry requires to make use of ingredients such as alcohol and

ether, which are under excise control, the Government will go to the greatest trouble to arrange matters in such wise that no needless restraint is imposed. That the staff of a Government department should interpret a Government order in an unduly restrictive sense, so that an industry might thereby be hampered, is there inconceivable. Only in Great Britain and Turkey are Government restrictions allowed to be interpreted at the will of the permanent officials. I do not for one moment wish to imply that I consider that the question of industrial alcohol has been of the main, or even of serious, import, compared with others, in our neglect of the fine chemical industries. I quote it rather as an example of the contemptuous attitude which our Government has hitherto adopted towards matters industrial. In certain branches of the chemical trade it is essential to have the chemically pure alcohols and ethers, but the would-be manufacturer is told, by the Government, in effect, that he is not to be a judge of what is necessary, but that the question will be settled by some heaven-sent genius in their permanent employ who, like the journalist on a halfpenny paper, knows more about the subject than the man who has made it a life's-work.

A feature of the German industries is their willingness and ability to work in co-operation, as is shown in many ways which are no doubt familiar to most of you, but with which we have not time to deal. With all the help which a favourably-inclined government could render, the German industries would have been unable to approach their present standard of efficiency had it not been for the remarkable co-operation which takes place between science and capital. This can perhaps be best illustrated by means of some concrete examples. Let us suppose that some chemist in Germany has discovered a new and cheaper method for making some chemical product which is in considerable demand, or which might become a large article of manufacture if the price were sufficiently low. If the manufacture is likely to require a considerable capital, the inventor would probably go to one of the large banks. The German banks permanently retain the services of some of the leading authorities on a wide range of subjects, and the inventor would be asked to put all his case before the particular expert in charge of his department. If the report were of a sufficiently satisfactory nature on the scientific side, the bank would proceed to make their own inquiries, through the many channels open to them, as to the probable outlet for the

new product. If the outlook were in all respects sufficiently satisfactory, they would advance the necessary capital at a reasonable rate of interest, making certain stipulations such as that the business should be carried through their bank ; that payment for the finished products should be made through the bank ; that no contract for the sale of the finished product should be made with any firm without their consent. The bank having much greater facilities for gauging the financial standing of the purchasing public, in this wise protect their own interests and that of the inventor.

Again, nothing is more startling to the Englishman than the ease with which one can gain admission to those in command of the great industries. The directors of the German companies, for the most part, and the managing director invariably, are men of high technical skill in the business they control. The idea of putting a stockbroker or a retired army colonel at the head of a scientific industrial concern would be regarded as an act of madness. Not only are German businesses run by men who understand them, but these industrial leaders have always time to give adequate consideration to any new proposal which is brought before them. It would be the exception rather than the rule to find directors in an English company who were capable of appreciating, still less of judging, the merit of a technical point relating to their own business. It would be almost an impossibility for an unknown outsider to obtain admission to such directors, and even if the unknown inventor succeeded in getting within the veil which hides the holy of holies, it would probably be to find that the master-mind had so many appointments that he never by any chance had time enough to consider any proposal thoroughly. The heads of a German concern have always time to look thoroughly into anything which interests them ; they are sufficiently technical to realise the necessity for going into details, a works experience having taught them that it is on details that great processes come to grief. In spite of their intellectual and commercial attainments, however, these directors are, in some respects, both modest and unassuming. They still think that success can be purchased only at the cost of labour ; they are content to work from 8.30 to 6.30, with two hours' pause in the middle of the day, and they work full six days to the week. No doubt they envy, but they do not lay claim to, that super-type of intellect which, labouring hard from eleven till four with an in-

terval for rest, sometimes even five days a week, expects, not only to retain its old position, but to dispossess its competitors ; they even learn foreign languages so that they may profit by the knowledge gained by other people in other countries.

Let us suppose for one moment that it was Germany that was short of drugs, photographic chemicals and dyes, and that England had possessed a monopoly in these products. Further, we will suppose that the joint general manager and head chemist of one of the large English drug and photographic chemical works had found himself in Germany at this period, with sufficient acquaintances in that country, men with whom he had for many years made large contracts and who were fully cognisant of his scientific and technical ability to guarantee his claims. He could go to any bank and say : "I can show you how to make a number of photographic chemicals and drugs even more cheaply than they can be made in the country which has hitherto controlled the manufacture, because you have the necessary raw materials, because you have, indeed, previously sold these raw materials to the previous makers. I bring you the necessary evidence that these products can be made at half the sales price obtaining before the war, and I can demonstrate that the sale in your own and neutral countries of these products amounts to some thousands of tons per annum, and that, under normal circumstances, after the war is over, it will be impossible for your business to be displaced by undercutting. Finally, I will bring you reputable dealers who will make contracts for hundreds of tons of these products at prices which will pay for the plant and show profits in one year's working." The bank would confirm these statements through their experts, and probably within forty-eight hours all the money that was required would be available at  $7\frac{1}{2}$  per cent. The man who possessed the scientific, technical, and commercial knowledge would thus be enabled to build up a business which would be profitable to himself and valuable to the community, the fact being that it is recognised in Germany that capital is entitled to a fair return and nothing more.

Now let us imagine that circumstances were reversed. It would require the pencil of a Hassall adequately to depict the scene in the board-room of an English bank where such a proposal had been made. One can imagine the possessor of such knowledge offering it to existing chemical works.



Modern commerce is warfare, and the weapons employed are inventions, tireless industry, skill, and capital. We make the mistake of putting the last first. Those who do research and make inventions, whether in chemistry, engineering, or any other branch, are the yeast which leaven the whole mass, but in this country we do not allow those conditions of warmth which permit the yeast to work. Gold in itself is not nearly so valuable a metal as iron, and we are slowly but surely finding out that capital itself is an over-valued possession if it be not used for the benefit of the industries and consequently of the nation as a whole.

### DISCUSSION

The Right Hon. Lord-Justice MOULTON said that he had had allotted to him for several weeks past the business of investigating into the question of the supplies of articles which in peace time were imported from Germany. First and foremost of those had been the problem of the great chemical trades, especially the great industry in synthetic dyes, and he had had an opportunity of marking in detail those things in which England had allowed herself to be supplied in chemicals from Germany. He could assure the audience that he had noted the fact with great sadness, and, he was bound to say, it was a great national humiliation. The fact was that chemistry opened up, especially some fifty years ago, a domain of industrial wealth which he could only compare to the domain which was opened up when steam power was first invented; and to his great sorrow he could come to no conclusion but one, and that was, that either from being too well off, or from sluggishness of intellect, or from the fact that the capital of the country had passed into the hands of people who were unwilling either to learn or to think, England had abstained almost entirely from attempting to reap the rich harvest that was opened to the industrial world by the advances in organic chemistry. The fact was too well marked for us to pass it by as being a mere incident in national life. Of course, no one thought that every nation could do everything; and that nations should, to a certain extent, specialise, should take advantage of their natural position, and the deposits that they found in their land, their climate, and things of that kind, was not only normal but desirable. But thought depended on no climate. Thought was open to us all; and the fact that England

neglected the chemical industries could not be explained away by any suggestion that it was either incapable or for any natural reason unfitted for their pursuit. One had to look deeper than that. One had to find some fault either in the national character or in the national behaviour which would account for it ; and he did not believe that England could, after the war, survive as a great industrial nation if she did not correct that fault, if she did not make an effort to take her place—and that an uppermost place—in the world of industry in chemical matters as well as in all others. If the conclusion was come to that it had been by a national fault that we had missed it in the past, and that we were not going to live a disgraced life in future, it meant that that fault must be found out for the purpose of avoiding it, and there, he thought, a lesson might be taken from our enemies. To his mind by far the most glorious moment in the history of Prussia was not the moments of her military successes—it was the moment of her deepest disaster. Those who knew Prussian history would remember that after the nation had been prostrated by Napoleon in the Battle of Jena the national independence was utterly taken away. The restrictions the conqueror put upon them were humiliating in every way. At that time there arose a set of men, of whom he chose to name, first, Fichte, who told the Prussian people in the clearest language that their disaster was due to their national faults, and pointed out the way that they must correct these ; and in the most unsparing language he told them that it was only by self-discipline, only by taking to heart their disaster, seeing in it the natural consequence of their national faults, that they could possibly get the resolution or the strength to replace their nation in the position which it ought to occupy. The whole nation listened. It was at that time that the Germans took to physical development and voluntary drilling. They prepared themselves in every possible way for that coming fight which they hoped they would have with their oppressors, and which they had in the course of a very few years, but they did it under the exhortations of these men, because they did not attempt to hide from themselves that it was the nation that was to blame for its misfortunes.

The fact that our chemical industries were in such a backward state, with certain exceptions of those which needed least thought and least study and least knowledge, was grave enough, if, as

he said, it was due to our national faults—it was grave enough for us in these days to rouse ourselves as the Prussians did rather more than one hundred years ago. He was quite sure that if we did do it the same result would come—that we should regain our position, and regain it with even more glory than it possessed before. There was a time when in no industry could England look on other nations as its superior. Now, in the chemical industry—by which he meant mainly the organic chemical industry—it was all but insignificant, and he read with very bitter feelings an address of one of the ablest industrial chemists in the world, the head of the German chemical industry, who was talking about the very subject, and who said : “England talks now of not only holding her own in war, but beating us in our chemical industries. She cannot do it, and that is because the nation is incapable of the moral effort to take up an industry like that—which implies study, which implies concentration, which implies patience, which implies fixing one’s eye on the distant consequences and not considering merely the momentary profit.” When he read those words he asked himself, Was that not a fair judgment for a foreigner who could not know the resources of the English people in the way of repentance and resolution and reformation? Was it not fair for that gentleman to say that our behaviour during all these years showed that we were incapable of doing it? And he would tell them frankly, that if we did not take the lesson to heart at the time of this war, and when the war had passed—when, as we believed, we should have severed ourselves from the military domination of Germany—resolve to save ourselves from industrial domination, all he could say was that the victory of Germany, if not in the form that it would desire, would be quite as great as it could wish.

Sir WILLIAM A. TILDEN said he had listened with mixed feelings not only to the paper but to Lord Moulton’s remarks. He could not help hoping most sincerely that the words which had been used by Lord Moulton would find an echo in those regions inhabited by the leaders of British industry; for it appeared to him that unless a good many of them first of all were brought to acknowledge their position of humiliation, and secondly, determined that if they were too old themselves to learn, at any rate their sons and successors should be taught what was necessary in the way of scientific instruction connected with their own businesses, then it was all over with British industry. He must

say out of his own experience, living as he had for fourteen years in a great industrial centre, that many of the author's pungent remarks were really not exaggerated. He used to see, with great regret, young men driving to business in the morning at eleven o'clock when the works had been going from six o'clock. In many works which he had visited he invariably was amazed at the extraordinary ignorance displayed on the part of the partners themselves in the operations which they were supposed to conduct in their businesses. Over and over again he had been in works in the Black Country, and his friend, the director or manager, was exceedingly anxious to show him anything ; but if he asked any question about details the manager or director could not answer them, but sent down the yard for "Old Tom" or "Old George," who was the only person in the place who seemed to know how the process could be conducted. He did not believe that the serious character of the question of education had yet been completely realised by the present industrial directors and leaders, and he could not help thinking that that was one of the most important considerations to be taken into account at the present time—that the young men who were to be the manufacturers of the future should have a very different kind of career from that which had been hitherto prevalent.

Dr M. O. FORSTER said, whilst fully agreeing with the author in his castigations of the manufacturer and the Government, yet he did think that while chemists were so busy in casting motes from other people's eyes, there was one beam in their own which certainly should be removed forthwith, and he thought the present opportunity was the right occasion to remove it. They had too long allowed confusion in the public mind as to what really chemistry was, and what chemists did. It was perfectly ridiculous that any attempt whatever should be made to capture German trade while the general public had not the faintest idea of the difference between the chemist and the druggist. At the present time the only people who were entitled to call themselves chemists were those who had undergone a course of training at the Pharmaceutical Society or who had passed examinations conducted by that body. In fact, he believed, of all the chemists, so-called, present that evening, only Sir William Tilden was entitled to call himself a chemist by law. In Germany and France chemists and druggists were clearly defined.

Dr RUDOLPH MESSEL thought that we as a nation had

been blind, so far as new chemical industries were concerned. We had everything ready at our hand. At one time there was a great deal of grumbling about education in science. He had been in England for forty-five years, and he could well speak about the enormous progress which had been made in this country as far as chemistry was concerned. There was talent enough, capital enough, raw material—everything. But what was lacking was enterprise. If the talent which was now available in this country was utilised, the industry would do just as well here as in Germany. He had to give one word of warning in establishing new industries—first of all to be sure that we only took up those industries which we were prepared to defend when war was over.

Dr F. G. OGILVIE said that the deplorable condition to which the author had drawn attention was not at all peculiar to the chemical industry; it has been observable in a great many other industries. There had been a tendency in connection with many individual industries for the divorce of the control of capital from the knowledge and experience required to apply capital effectively. It arose in the following way—a man had done very well, say, in the manufacture of tweeds in a centre where a large tweed industry was going on. His family found themselves very well to do, and were attracted, as young men, much more to field sports, county meetings, and things of that sort than they were to the serious study of their own particular business. The net result was, when they came into power they had to work the business by managers, often underpaid and undertrained, who naturally, even when they proved themselves very good men, had not the ready access to the application of capital year in and year out which was necessary to keep the business up to date. This did not happen where the sons had added scientific training to practical experience in the works. In that case there were good, solid, steady-going businesses which were introducing new products just as fast as could be wished.

Mr ADAIR ROBERTS said that many of the businesses which it was now sought to capture from Germany could be started with very little capital.

Mr WALTER F. REID said he thought it was quite impossible to suggest that a young chemist, just out of a college or university, could get a large salary unless he showed himself to be worth it. An employer would look at him as a beginner from

the industrial point of view. In fact, he was an apprentice, and if he was not willing to take the salary of an apprentice at the beginning he could not grumble at the capitalist, who opened up to him a very good future of great promise. With regard to the glass industry, we had lost that industry chiefly through the unwillingness of the workers in the trade to allow apprentices in sufficient number. After the production of capital, the next important point was the security of it. He could not put the matter more clearly than it was put by the Institute of Chemistry, which said, "Provided that the manufacturers could be afforded some guarantee of permanency for their enterprise, and that they may have some reasonable assurance that at the conclusion of the war the newly developed industry will not suffer from foreign competition, hitherto made possible by economic conditions which do not prevail in this country." Dr Messel had said exactly the same thing. If the capital which would have to be invested in new and expensive plant and in the payment of research workers and other workers could not be secured, then the capitalist could not be blamed for not coming forward. Our workmen and capitalists must be given the same protection as Germany gave to theirs. Our German competitors could then be met on equal terms, and he was not afraid in the least what Englishmen would then do.

The Lecturer said he agreed absolutely with Dr Messel that we must be most careful to take up only those industries where we were at least on as good a footing as the Germans were with regard to raw material. With reference to workmen, he had not the slightest doubt that English workmen were better than any other workmen on the face of the earth. But up to the present neither the English workman nor the English chemist had been given half a chance to handle modern scientific processes. It was the opportunity to let each of them prove what he could do that had been lacking.

Mr W. H. MAW said that the state of affairs which the author had described as existing in the chemical industry also existed in past times in many other industries. In the case of the engineering trades and iron and steel manufactures the last twenty years had seen a very remarkable advance in the recognition of the value of scientific research, and he hoped the same advance would take place in the chemical industry.

XXVI.: 1914

## THE MANUFACTURE OF ANILINE DYES IN ENGLAND

BY THE RIGHT HON. LORD-JUSTICE MOULTON,  
P.C., K.C., F.R.S.

(Address delivered in the Town Hall, Manchester, on 8th Dec. 1914)

SOME weeks ago now I was asked by Government to take the Chairmanship of a small Committee that had to investigate the straits into which England was put by being cut off from that great supplying nation, Germany. I have had to investigate all the unsatisfied wants that have sprung from this war, and I am glad to say that in almost all the cases which cropped up—so numerous at first—it has been found that the resources of English enterprise were sufficient to meet the demand; that some makers have been more attentive to the variety of the tastes of their customers; that others have increased their works; that others have added new branches to their business; and that the straits have been alleviated if not removed. Everything that has happened has placed in harsh and dissonant contrast the question of dyes. Nothing that I have seen during these weeks—and I can claim to have spent almost every hour of the day in meeting the members of the trades affected, and in trying my best to find some way out of the difficulties—nothing that I have seen in these long weeks has weakened, nay, I can say nothing has failed to strengthen, my feeling of the gravity of this problem.

The consequence is that after long reflection I have come to certain conclusions, and I have not hesitated to place them in the clearest language before the Government. Now the Government has taken an unusual and almost unprecedented step in the direction to which I refer. I am not responsible for

the details of that step. I am not in any way connected with the shape or form in which the action is to take place otherwise than so far as it has been a necessary consequence of the advice that I have given. The one thing I am responsible for is that advice, and I stand here not as the representative of the Government, not as an advocate of a particular scheme, but to give you the same advice, based upon the same considerations, the result of the same reflections. Although that is a strange position for a man who is speaking in public, it is no strange position for me. There are the faces of many here in the audience who in years past have come to me for advice ; who have asked it and taken it ; who have shown by their coming that they had faith in my judgment. Well, I hope that faith has not entirely passed away.

But in any case I am coming in the attitude of one who is giving advice. When I used to see them in my rooms at the Temple I would as soon have thought of chanting my opinion as trying to put it in eloquent words. It will be the same to-day. I shall put to you in plain business language the things that have haunted me for these weeks past ; things that have oppressed my thoughts day and night. In my opinion we are at a crisis of our national life, and I shall try to put as plainly as possible, in the simplest words, the facts which have led me to that conclusion.

When I began to investigate the lack of dyes I found England consuming some two million pounds' worth of dyes per annum. They were essential to an industry of something like two hundred million pounds per annum, and on which at least a million and a half workmen were dependent. And I found that of the two million pounds' worth of dyes that was required year by year barely one-tenth was produced within our own boundaries. I looked round for industries which could at a pinch supply the deficiency. So clearly demarked from other industries is the great chemical industry of the coal-tar dyes that I could find no industry which could take its place.

I found that the stocks of dyes, the stocks kept in peace times—for no warning of the intended war had been vouchsafed to *English* customers—I found that those stocks were rapidly diminishing, and that practically there was only one nation from whom we could expect help. I refer to Switzerland, and I knew that in that country pressure was being put by Germany of the most intense kind—threatening to stop all those supplies of their



intermediate products on which the Swiss dyemakers had built up their business, unless they would promise that not a pound of their dye should, for the whole period of the war, come into this country. I found certainly some English firms who were manufacturing, and manufacturing successfully, in spite of the competition of the Germans. But what they could supply was indeed inadequate to keep going the great textile industries which ultimately depend to such a large extent upon the dyeing industry.

That was the serious immediate prospect. But what does the future promise? It is that which I have been brooding upon ever since. Supposing that this war was finished. Supposing that by the bravery of our soldiers, and by the unflinching determination of our Government and that of the Governments of the Allies, we come out of it politically free. What position do we step into industrially? We step into the slavery of the Germans, so far as our textile and dyeing industries are concerned, as absolute as they hoped to put us in a political and military sense.

What I am saying is no exaggeration. In my perpetual converse with those of you who are practically interested in the question I have learned the German methods of carrying on business. I know their way of dividing all the nations up into watertight compartments, by their system of selling dyes not to be exported, so that they can put the price up to one nation and down to another. I know the way in which even the two great rings, which may be competitors one to the other in Germany, are united against the foreigner.

I say gravely, meaning every word that I say, that if peace were declared at this moment you in the English textile industry would be so much under the domination of the German dye-producing industry that it could boycott you in the way of dyes, it could overcharge you for dyes, and it could hamper that industry pending the time when it had the capital and works to challenge its very existence. And as an Englishman, that fills me, I will not say with dismay—because I have a blind faith in my countrymen which makes me believe that out of the most difficult position they will, when they once realise it, pull themselves successfully—but it made me feel that it was my business to sound a note of warning, and not let people go on thinking that this trouble from shortage of dyes was one which would be

temporary, lasting only during the war time. No. It was a signal of danger which threatened us more in peace than in war, and if we would not listen to this danger signal then our fate was on our own heads.

Well, now, in most things you ought to consider how to do them before you determine to do them. But there are exceptions. This war was an exception. I do not think that many of us knew how we were going to struggle through this war, but yet I doubt if there is a man in this audience who did not feel that we must take it up. I feel about this industrial war just the same. I feel that the first thing we have got to do is to say to ourselves, "That shall not go on." And then we have to set to work to find out how we can stop it.

But to find out how we can stop it we must first consider what are the causes which have led to this strange position, that a great enterprising industrial nation—a nation which lives upon export industries—is in the largest of its export industries, which I believe produces one-third of the total exports, at the mercy of the foreigner. How was it that when the great chemical trade, based on the marvellous way in which coal-tar products will assume myriad forms and myriad different properties, when that El Dorado was discovered, far more valuable than the Rand ever will be, how was it that England did not have its share?

Was it discovered by foreigners? It was started by an Englishman. Was it that foreigners alone had the natural resources to carry it on? For years practically all the raw materials wanted for this industry were sent out in an untreated state from England. Then why was it?

Gentlemen, we have got to look the truth in the face. It was for no other reason than the English dislike of study. The Englishman is excellent in making the best of the means at his disposal, but he is almost hopeless in one thing. He will not prepare himself by intellectual work for the task that he has to do. Now in the last fifty years the knowledge of the world, the additions to that which we know, which have been piled up from the work of ten thousand independent investigators, each applying himself to one thing, have made it so that with regard to each subject there is a vast amount of the "known." And a wise man who means to deal with a subject will master what is known before he attempts the problem of what he can do. That is what the Germans, who were rightly ambitious, accepted as

the condition of success in industry. If you talk to any German who is engaged in any industry you will find that he knows about it all that can be known.

I admit that it does not make him a more pleasant companion. Once I found myself on the top of one of the Dolomite Mountains, and the only other person there besides the guides was a German. I found out that he was a chemist, and I began to talk upon a chemical subject. He told me he was only an organic chemist. He had not exhausted my resources, and I began to talk of coal tar and pharmaceutical products. Then he told me that he was a coal-tar by-product chemist. That did not beat me, because I had just been fighting a case of canary yellow. I thought I would get some subject which was common to us, and I slipped into the subject of canary yellow. Still the same ominous silence for a time, and then he said, "I am only a coal-tar chemist dealing with blues." But I had not finished. With an Englishman's pertinacity, not believing I was beaten, I racked my brains for a coal-tar blue—I had had to advise on some cases—and I gradually, without a too obvious change of subject, slipped into that. Then he finally defeated me, because he said in equally solemn tones, but equally proud of the fact, "I only deal with methyl blues."

That gives you an idea of the way that a German is willing to give up everything so as to concentrate on the subject with which he has to deal. It may limit his general view of life. I confess that it is almost worse than wearing blinkers. Goggles are the only thing I can think of which at all describe the mental limitations. But this makes the Germans most formidable in industrial questions. It makes them thorough in that which they have to do.

Now, apart from certain business methods which I may have to refer to later on, I believe the sole cause of England's falling back, and Germany's possession of this great industry, is the fact that the Germans are perfectly prepared to undertake the intellectual study necessary to master the new science. The English, I believe, could do it just as well, and you will find in their great works English chemists as highly respected as the German, and as efficient. But unfortunately the holders of capital in England have had little sympathy with knowledge that they did not themselves possess. As I have been talking these matters over with people—energetic, good, industrial producers

—I have always found that when I commenced to talk about the intellectual study necessary to deal with chemical science there has always been that tone recalling the voice of the sluggard, “You waked me too soon.”

They know the time is coming when they will have to do it, but they hope that during their time the traditional ways of their fathers may be sufficient, and let the next generation face the intellectual difficulty of study. The consequence has been that inventions—great inventions—have fallen dead in England. They have been offered in Germany; they have been studied by instructed minds; they have been accepted. And the consequence has been great industrial production, the fruit of which all the rest of the world has received. But in England, “Well, ah! yes. It has not been tried. It is difficult.” It is given to somebody who has not disciplined himself like the Germans do, and he finds difficulties, and then gradually the thing is dropped. For you must remember that because the masters, the heads, the capitalists, have not got sympathy with this self-preparation for the difficult tasks, there is no career for the young men who are willing to study. What can they do? They are paid salaries quite insufficient for the training they have to go through, and for the learning they have acquired. The consequence is, that when I am asked how it is that we are so poorly represented in the industrial ranks by chemists, I say, “Make a career for your young chemists, and then you will see.” We have not done so.

Now that is the cause, and, so far as is material, the sole cause, of the German supremacy. Remember that there is not one single thing in which we are at a disadvantage by natural position. It is perfectly true that in the Creation, by some blunder, the most valuable deposit of potash was put in the centre of Germany, but we can get potash from elsewhere if we want it. As to coal, and the sources of the coal-tar industry, we have them in richer quantity than even Germany itself. The one thing is the difference in the human element, and this is not a difference in intellectual capacity, but in the industry and in the willingness to study to the bottom the subject with which you have to deal.

Gentlemen, that is my opinion of the cause of England's inferiority, and I ask myself at once, “Is that a cause which must permanently operate?” The answer is, of course, “No.” But it is for us to reform ourselves. Otherwise no relief can come.

It is impossible that we can get a chemical industry like the German's unless we are willing to train ourselves for it, to have faith in it, to embark our capital in it, and in this way take the steps which lead to it. Consequences follow causes in this world; and to hear people grumble at this difficulty about the dyes when one thinks they have neglected all the necessary causes to produce the industry, would make me feel almost impatient if it did not make me sorrowful.

The question is, then, has the condition of things become so permanent that it is too late to do anything? Here I confess that I feel cheerful. Let me deal for a moment with the difficulties that appear to one. The first is that there is a lack of the necessary technical skill. I have a great difficulty in returning a polite answer to that. To my mind it is nonsensical. We have the command, and we shall in peace still more have the command, of abundant technical skill to create the industry. You must remember this, that in the long catalogue of dyes (over which I have been poring all these weeks) the vast number are dyes the processes for the manufacture of which are well known. I do not say that the man who is practised in it will not get a better yield, or that his handiwork will not be more certain. Of course it will. But there are no people better qualified to learn by experience than the English people themselves, and the whole of these dyes can be manufactured with as great certainty in England if we put up the proper plant and choose the proper men to guide it.

Now let me go to the more recent dyes, those that have hardly made their way into commerce, but the qualities of which show that they will be very desirable. It is perfectly true that if you want to manufacture these on an industrial scale you will previously have to study in the laboratory, by observation of the reactions, how to get the best results. But you will be astonished how few the processes are in this great industry, and the extent to which they are simply the repetition of the same processes with different substances and under different conditions. The sole difficulty which separates brilliant success from comparative failure is that study has shown how to regulate the conditions so as to make the results most favourable.

There is no mystery to the chemist. There is that which requires study before he can arrive at it; but if you are going

to be daunted by that, then the rest of my speech will not interest you. So that the objection of not having abundant technical skill to carry out any industry that we form is in my opinion absolutely baseless.

Well, then I am told, "It is impossible to compete. There are works with a capital of a hundred millions in Germany. Your foes are willing to crush you by every means they know, and those means, I can assure you, are various and effective."

Well, that is a very great fact, but if you tell me that it is impossible for manufacture to go on in spite of this competition I will ask you to turn your eyes not only to this country, but even to Germany, where you find firms outside these great combinations, who in their own particular line have a successful business, and even an export business, in which they contrive to flourish—not to make the gigantic profits of the rings, but still to make fair industrial profits. In your own country you have them. You have firms that in spite of the pressure of the Germans manufacture at a profit. And side by side—if you look back—with these firms there were many other firms whom the Germans feared sufficiently either to buy out or to crush out. When they realised that they were capable of producing in competition with them they felt that at great cost they must get rid of them. That, surely, is proof that competition in production is not impossible.

Remember this, that success in production depends no doubt on cheapness, but if you produce on what I may call an economical unit, that is on a scale which is adequately great, the advantages from doing it on an enormous scale are very small in comparison. And certainly England, with its rich market, its demand for dyes—and many of these demands capable of being satisfied with comparatively few dyes,—England can certainly start an industry in which the manufacture is on such a large scale that it can challenge if not equal the economies of the biggest works.

Let me now go to the third objection which is raised to the possibility of our competing, and it is raised in connection with the suggestion that I am defending here—the consequence of my conclusion that a great national effort should be made, and a large company formed capable of producing dyes on a scale sufficient to satisfy the English demand. It is a very curious one, and yet you have all heard it. I remember saying to one

with whom I was discussing the matter, and who knew well the trades of Lancashire and Yorkshire—"Don't you think it would be of infinite value to England to have a company which would for ever secure its dyeing and textile industries, aye, and the great pigment industries, which must not be forgotten, from being overcharged for their dyes?" The man said, "But that is not what I am thinking about. I am not thinking about being overcharged. My fear is we shall be undercharged!"

Here I was trying to protect an English industry. I was talking to a man vitally interested in it, and what was his fear? His fear was that the consequence of our doing it would be that you would get dyes cheaper than they could be made, and that was what was frightening him. I will tell you what it reminded me of. Supposing there was a question of building a defensive fort to protect the vital part of a country, to protect, we will say, London, and the objection was raised, "Oh, but if you build it as strong as that nobody will attack it, and then how will you defend the spending of your money?"

I ask you to think of this objection seriously, and in the light in which I am putting it to you. To my mind it is the most universal and the meanest of all the things which influence men's minds on this subject. They are afraid it will be too successful. They know that if they do not make such a company they will be ruthlessly overcharged by the Germans. Of that there is not a fraction of doubt. They know that if they do form this company that cannot be so, and the probability, they think, is that your great industries will have their dyes cheaper even than they can be made. They must realise that that, to a nation which has a world-wide commerce, is a boon beyond estimation, and yet they are afraid, if they put their money in, that they will win this boon for their fellow-countrymen.

What does it mean? It is that ineradicable defect of the English mind, if it has not by travel or study or reading got rid of its insularity. I used to sit for a constituency, an agricultural one in the South, and I never could get out of the head of any one farmer that his real competitor was the man living next door to him. He did not realise that this insular idea of being afraid that the man next door will get the better of you for a penny, or that his goods, which are not quite as

good as yours, will still be treated alike with yours, is the thing which has prevented all co-operation among them in the south. While Denmark, a poor country, has been rolling up its wealth by combined action, our English people stand apart, and are still as unfitted for helping the wholesale trade of the world as if it were almost fifty years ago.

What this objection means is, you are afraid that Mr So-and-So, who has not subscribed, will get all the benefit you have won by your subscription. You do not doubt that you will win it for your country. You do not doubt that you will win it for yourselves. You do not doubt that in this way, so far from industries being harried, they will be put in an undeservedly fortunate position. And yet you do not want to do it because the gain will come to your trousers pocket instead of to your waistcoat pocket. Instead of coming in dividend it will come in the lower price of dyes.

So, if I could believe that the formation of this company would force the Germans for one year or two years or twenty years to sell their dyes at less than cost price, I should come to you and say, "You have got a chance now to save yourselves and England, and to put yourselves and England in a position of vantage in competition in foreign lands that you have not deserved but that you are going to get."

But, gentlemen, I frankly tell you that I do not think you are going to have such a good time as that. I will tell you why. If a great company is formed that is efficient and that produces, as an efficient English company will produce, at fair prices, it will cost the Germans too much to sell below cost price here. For this reason : once satisfy the English market with these low-priced dyes, and you free the output of this company to go to those Eastern markets, out of which the Germans derive the profits which enable them to fight you, and you can sell there at fair prices, and the Germans will either lose the market or there, too, they must drop their prices.

I think you will find that dropping prices all round is not a good way of increasing your profits. You are business men. I am not a business man, but my opinion is that they will find that it is better to leave you alone, better to leave you to supply yourselves than to set free such a formidable output as a great company would make to compete with them in the other markets of the world.



What does all this lead to? It leads to this. In my opinion there must be, in order to give England industrial freedom in this group, which is almost, I should think, or quite, the greatest group of its industries—there must be a great national effort to create a company, a company working under the conditions of other companies, suffering from its blunders and profiting by its wisdom.

But there are three conditions, and unless those three conditions are all satisfied it will be a failure.

The first condition I lay down is that it must be large. Politically, the Germans are frankly the foes of small nations. They consider that small nations are to be eaten up. Industrially, this great embodiment of the German idea, the combination of the dye manufacturers, behaves to small manufacturers exactly as Germany seeks to behave to small nations. It is hopeless to suppose that if there are sporadic attempts, all small, they will not be either dragged into a combine, or crushed by a combine, or in one of the many other ways, which you all know, put out of existence. It must be large, and therefore independent, and therefore beyond attack.

There is another thing. It must be national in this sense: it must be removed for ever from the temptation of listening itself to the voice of the charmer and entering into a combine.

We must have a company that is not only powerful, but one the loyalty of which is necessarily beyond all doubt, and that we can only get if it is assisted by the Government, on the terms that the Government can stop it from ever entering into the backward path which would ruin its national utility. Most of you like the idea, I can see, of its being large, and of its being kept always true and faithful to its national aim.

Now I am going to tell you the third condition, which concerns you. It must be co-operative. The producer must be the consumer. You will never link up all these industries unless those who use the dyes are included, the textile people as well as the dyeing people, and those who are in the great pigment trade. Unless all those who are about to consume have an interest in the production, and therefore supply a preferential market, you will never succeed in making the company relieve the national need. If I had had the millions I wanted offered me on the Stock Exchange for a company which would be free from all trammels, which would have no connection

with the trade, the shares of which would be bought as the others that are called industrials on the Stock Exchange, where every penny of profit it made would be squeezed out of it for the benefit of the then holders of the shares, who would care nothing for the holders of the next year or for the future of the company, I would have said at once, "It is doomed to failure," and its failure would be only the more marked because it was gigantic.

You must realise that you, the consumers, should loyally all combine with the producing company, and then I will defy the German or any other competition to break down that bond of union. Remember this. The only thing which will ensure a combine or a ring against failure is co-operation between the producer and the consumer. I remember one of the earliest cases that came before me. It was a case of a very great industry, and we were told that it was entirely in the hands of such a ring formed in such a city in Germany. Well, what happened? We got the producers and the consumers together and said, "If you will produce the article yourselves you can defy rings. How can they touch you? (It happened to be a question of a metal.) You can buy in the markets of the world. It is produced everywhere. No one can run up the price against you, and therefore the worst that can happen is that you are on equal terms with them."

Now some of you will say, "Oh, yes, but is not this a violation of the chief commandment, 'You shall buy in the cheapest market'?" Is it? Remember this, that in considering what is cheap you must not look at the money that passes, but at the consequences of the purchase too. The man who says, "I will buy for five years at a discount of five per cent., with the certainty that I shall have to pay fifteen per cent. more for the next ten years," and thinks he is buying in the cheapest market, is, I suggest, a bad student of economics. It is not buying in the cheapest market if you buy something which destroys your real security for cheapness, which prevents you from being overcharged. And I am perfectly certain that when the idea of loyal co-operation gets hold of Lancashire and Yorkshire the foes of England in the industrial world will begin to tremble. We have had a time of peace in England, and we have never thought of dangers industrial or national. But there are these dangers, and even though there may not be another war, as we trust there will not be, there is perpetual war going on industrially, and it

is not based on the ideas of each man doing his best and of fair sale and fair purchase. It is based on what in the industrial world corresponds to war in the political world, and if you do not realise that, if you will not stand by one another as producer and consumer, and you let the producer go down under his enemies, so that in turn they have the mastery of you, then all I can say is that as consumers you have been buying in the dearest market, and you will deserve the consequences that you get.

Now, gentlemen, I have come to the conclusion of which I told the Government. I have nothing to do with the particular form in which the Government have followed out that for which I am responsible as an adviser. You must have a large company—a company with national control so far as to keep it in the right path; and you must have a company which is co-operative between the producer and the consumer. If you do that, I can warrant it a long and successful life; but if you attempt to leave out any one of these three essentials, it is predoomed to failure.

Just let me say one or two words in conclusion. Supposing our War Minister had been in the last few years buying in the cheapest market for the sake of cheapness, and that he had had the munitions of war manufactured by Krupps, of Essen. Gentlemen, I think he would have been lynched about three months ago. You would have realised when the moment of need came that your sources of supply were cut off. Now, gentlemen, there are munitions of peace which are essential for the defence of the great industries of the country, which are vital. There are munitions of peace as to which you have to take the same precautions as in regard to munitions of war.

You have to realise that, so far as it is possible, a country should be in such a position that if its supplies are cut off, for any reason whatever, from outside, it should be able to supply itself. Of course, we realise that in raw materials and in many other things we must depend on supplies from outside, and that is the reason why we are a nation that spends so unstintingly on its fleet. But this is no question of getting raw materials from a foreign country. It is a question of being at the mercy of a country, not friendly disposed, in a matter where we could make ourselves independent; and it is a case in which we know perfectly well what are the morals of that country in regard to

its behaviour to other nations. Therefore I say you must look upon it as if it were one of those necessary munitions of peace which you must see adequately manufactured among yourselves.

Some will say—there is none here, I trust—what I heard of a great dealer saying, “Oh, but I am a business man. I only look at things as business propositions, and a tenth of a penny would make me buy everything from Germany rather than from England.” At that very moment tens of thousands of men were exposing their lives in the trenches to protect that man and his money. I wonder how many would have been there if it was always thought a brilliant thing for a man to look on everything from the point of view of a business proposition?

If that is being done by the recruits, what are you and I going to do for our country? You cannot go to the trenches, and yet I believe you are all willing and burning to do what you can for your country. Well, this is your part. You can protect your country by taking care that when peace comes it shall be under no subordination. That is what I ask you to do. A great writer has said, “There is nothing more desirable in life than to be wise at a great moment.” This is a great moment. Be wise.

XXVII.: 1915

## GERMAN CHEMICAL INDUSTRY THIRTY YEARS AGO

BY THE RIGHT HON. SIR HENRY ROSCOE, F.R.S.

(*Journal of the Society of Chemical Industry*, 30th January 1915, p. 65)

THE following short report, written by myself for the Royal Commission on Technical Instruction, of which I was a member, was printed in 1882. This shows that even in those early years the Germans had seized upon the methods which have made their chemical industries so successful, and that money cannot secure success unless it is accompanied by perfect scientific method, and above all by the recognition of the importance of original investigation :—

### ON THE INFLUENCE OF TECHNICAL EDUCATION ON CERTAIN BRANCHES OF CHEMICAL INDUSTRY

We have here collected our notes on certain special industries, viz. (1) chemical colours, (2) beet-sugar, and (3) the alkali trade, upon which the influence of technical education is plainly observable.

#### *Influence of Technical Training on the Chemical Colour Industry of Germany and Switzerland*

Among the coal-tar colour works visited by the Commissioners were those erected on the banks of the Rhine at Basle by Messrs Bindschedler & Busch. These works, though far less extensive than those of Messrs Meister, Lucius & Brüning, at Höchst, or of the Baden Aniline and Soda Works at Ludwigshafen, are

carried on in a no less scientific spirit, and the general method of working adopted in all these establishments is identical.

The first principle which guides the commercial heads of all the Continental colour works is the absolute necessity of having highly trained scientific chemists not only at the head of the works, but at the head of every department of the works where a special manufacture is being carried on. In this respect this method of working stands in absolute contrast to that too often adopted in chemical works in this country, where the control of the processes is left in the hands of men whose only rule is that of the thumb, and whose only knowledge is that bequeathed to them by their fathers.

On entering the works of Messrs Bindschedler & Busch one is struck, in the first place, with the adaptation of means to ends, with the substantially built, well-lighted, well-ventilated workshops, and, above all, with the all-pervading cleanliness and neatness. But it is not of these things that we now desire to speak, but rather of the method by which their business is conducted. In the first place, then, the scientific director (Dr Bindschedler) is a thoroughly educated chemist, cognisant of and able to make use of the discoveries emanating from the various scientific laboratories of the world. Under him are three scientific chemists, to each of whom is entrusted one of the three main departments, into which the works are divided. Each of these head chemists, who have in this instance enjoyed a thorough training in the Zürich Polytechnic, has several assistant chemists placed under him, and all these are gentlemen who have had a theoretical education in either a German university or in a Polytechnic school. An important part of the system has now to be noticed, viz., that directly under these scientific assistants come the common workmen, who have, of course, no knowledge whatever of scientific principles, and who are, in fact, simple machines, acting under the will of a superior intelligence. The many and great advantages of this arrangement are patent to all; and the fact of having men of education and refinement in positions of this kind renders the foreign manufacturer who adopts this system less liable to annoyance and loss (from sources which we need not more nearly specify) than his English competitor, who works on a different plan.

So much for the *personnel* of the works. Now for the mode in which they carry on their work. To begin at the beginning,

we find no less than ten well-equipped, airy, experimental laboratories in these works, perfectly distinct from the workshops where the manufacturing processes are carried on. In these ten laboratories, the chief departmental chemists and their assistants work out their investigations respecting the production of new colouring matters, or the more economic manufacture of old ones. To assist them in their work, a complete scientific library is at hand containing all the newest researches, for these, as we have said, form the material out of which the colour-chemist builds up his manufacture, and no sooner do the results appear of a perhaps purely scientific research which may possibly yield practical issues, than the works-chemist seizes on them and repeats these experiments, modifying and altering them so as at last to bring them within the charmed circle of financial success.

Thanks to Dr Bindschedler, we are able to quote a specially representative case, and a clear description of one such case is worth a host of generalities. Through the original investigations of Messrs Emil and Otto Fischer, the attention of the manufacturer was drawn to the leuco or colourless base obtained by the action of benzaldehyde on dimethylaniline, inasmuch as they stated that the salts of these colourless bases become green on exposure to air. Founded on these observations, an endeavour was made to effect the practical manufacture of a green colouring matter by oxidation of these colourless bodies. In order to attain the desired end, the following investigations had to be made by the chemist and his assistants who were to conduct the operations:—

(1) A cheap method had to be found for manufacturing benzaldehyde.

(2) A profitable mode of making the leuco base had to be worked out.

(3) The proper oxidising agents and their best method of application had to be determined.

(4) The best method of purifying and of crystallising the green colouring matter had to be discovered.

The laboratory experiments on the above points having proved so far successful as to give prospects of good results, operations on a somewhat larger scale were started, and these yielding a satisfactory issue, the manufacture proper of the colouring matter, now well known as malachite green, on the technical scale was commenced, all the operations being watched by and constantly being under the control of the chemists. But

even now their scientific work is by no means ended. Continuous laboratory experiments go on for the purpose of finding improvements in the mode of manufacture. Thus, for example, the improved yield, both as to quality and quantity, of the benzaldehyde is a matter of investigation. Again, the synthetic production of the pure leuco base by a more direct process is sought for, so as to get rid of loss in working, and to obtain a yield as close as possible to that pointed out by theory. In the same way improvements in the materials used for oxidation, and in their application, are made, so as to effect the oxidation quantitatively, without the formation of by-products. Lastly, the action of various solvents is examined, so as to obtain the best form of the crystallised colouring matter. As indicating the value of these improvements made after the colour became a marketable article, it is only necessary to state that the price of the crystallised oxalate has been reduced from £2 to £1, 4s. per kilo.

The foregoing may serve to give a picture of a really scientifically conducted works, where each step in advance is made systematically, as the result of a well-devised plan of operations. This is, indeed, the only means of progress, and this fact is so well recognised in Germany that each of the much larger colour works at Höchst and Ludwigshafen possesses a staff of from thirty to forty well-paid and thoroughly trained chemists to conduct their operations.

But we are, of course, far from believing that because the methods adopted in these foreign colour works are scientific and productive of good, those made use of in all English works must therefore be unscientific and bad. Taking the whole applications of chemical science we may, no doubt, with truth say that the English industrial chemists have been at least as successful commercially and certainly as productive in new and important discoveries as their Continental rivals. The Germans and Swiss, however, have been and still are distinctly before us, not only in the facilities which they possess of obtaining the highest technical training in their numerous universities and polytechnic schools, but what is even more to the point before us, is the general recognition of the value and importance of such training for the successful prosecution of any branch of applied science.

The following statistics give some idea of the magnitude of the colour works of Messrs Meister, Lucius & Brünig,



at Höchst, near Frankfort, referred to above, and founded in 1862.

The establishments occupy an area of 150 acres, of which 20 are covered with buildings. The staff includes 51 scientific chemists, 50 foremen, 15 managers and engineers, and 77 clerks and commercial men, with 1400 workpeople. The works possesses its own railways, 41 boilers, with a heating surface of 4000 square yards, and 71 motors, either steam, water, or gas engines. The workmen and officials are domiciled in houses belonging to the company, and restaurants, baths, sick clubs and pension funds have been established for the good of the employées. There is also a fire-brigade with 5 hand engines and 1 steam fire-engine. The total supply of water, from 145 fire-cocks, amounts to 30,000 cubic feet per hour.

In 1882 the products of these works amounted to :—

- (1) 6,600,000 lb. weight of alizarin.
- (2) 2,200,000 lb. weight of aniline oil.
- (3) 1,540,000 lb. weight of aniline, resorcin, and naphthol.

### *Colours*

The following are the separate products classed together under the last head :—

Aniline and aniline salts.

Fuchsine (no arsenic used in its preparation).

Methyl violet.

Green and blue colours.

Eosin colours.

Naphthol colours.

Alizarin and artificial indigo.

Quinolin derivative (kairin, a new substitute for quinine).

Acids.

The most important raw materials employed in manufacturing the foregoing products are as follows :—

40,000 tons coal.

3,000 „ tar products.

2,400 „ caustic soda.

400 „ potash salts.

2,900 „ carbonate of soda.

17,400 „ sulphuric acid.

10,100 tons	various other acids.
1,500 „	iron borings and filings.
250 „	wood spirit and spirits of wine.
1,000 „	various chemicals.
6,800 „	common salt.
2,050 „	carbonate of lime.

The whole of the sulphuric, hydrochloric, and nitric acids used is made on the works.

From about 70 to 80 per cent. of all the aniline colours manufactured are exported, the remainder being used in Germany.

About 90 per cent. of the total make of alizarin is exported chiefly to England, but considerable quantities find their way to America, Russia, France, Holland, Spain, and Italy.

One of the most recent and most interesting additions to the above list of products is a derivative of quinolin, termed kairin, lately discovered by Emil Fischer. This substance, which is now being made at Höchst at the rate of about 22 lb. daily, has been shown to possess important febrifuge properties, even exceeding quinine in activity, and it is not impossible that this artificial product obtained from coal tar may be the means of supplanting altogether the natural alkaloid. The importance of this discovery, should it serve the above purpose, can of course hardly be overrated, and it will then add another and most striking example to the numerous ones which already exist of the immense importance to the human race of researches in purely scientific organic chemistry, which at one time appeared to have no practical value or possible application. It may, therefore, serve again to point the moral, which cannot be too strongly insisted upon, that it is only by the highest and most elaborate achievements of pure scientific investigation that the greatest practical advantages to mankind can be secured.

XXVIII.: 1915

## THE MANUFACTURE OF DYESTUFFS IN BRITAIN

BY PROFESSOR W. M. GARDNER, M.Sc., F.I.C.

### I

#### A SUMMARY AND AN APPEAL

(*Nature*, 21st January 1915, p. 555)

THE speech of Lord Moulton in Manchester on 8th December 1914 was a notable event, even in these days of strenuousness and surprise. For although he was careful to disclaim any official sanction of the views he expressed, it was common knowledge that the Government had requisitioned his services in investigating the question of the shortage of dyestuffs, and had based its policy largely on the advice he gave as the outcome of his investigation.

The general outline of the crucial position in which the British textile trades are placed at the present time is well known. At least 1,500,000 operatives are engaged in the various branches of the trade, which has an annual value of £200,000,000. Nearly the whole of this vast industry depends for its commercial success upon the use of dyestuffs, which cost about £2,000,000 per annum, and only about 10 per cent. of the necessary quantity of dyestuff is made in this country. Before the war, between 80 to 90 per cent. of our dyewares was imported from Germany, and this supply is now entirely cut off. Unless, therefore, immediate steps are taken greatly to increase our national output and the supply from neutral countries (chiefly Switzerland), a catastrophe will very quickly overtake the great textile and associated industries.

The magnitude, gravity, and imminence of the crisis clearly pointed to the necessity for Government action, and a "Chemical Supplies Committee" was appointed to confer with the Board of Trade on the position. This committee included a number of well-known chemists, and manufacturers and users of chemicals and dyestuffs. The investigations of Lord Moulton and of this committee are understood to have formed the basis from which the offer of the Government was developed, but the committee was apparently not responsible for the details of the scheme for the establishment of a large Joint-stock Dye-manufacturing Company, which was made public on 22nd December 1914.

Prior to this, on 10th December 1914, a meeting of large users of dyes was held at the Board of Trade, at which a resolution was unanimously passed welcoming the assistance of the Government in a national effort to increase the British supply of dyes. A small committee, representative only of the users of dyes, was appointed, and elaborated the scheme to which reference has already been made for the formation of a manufacturing company.

An influential committee, appointed by the Society of Dyers and Colourists, has also made exhaustive inquiries on the technical side and has accumulated much valuable information.

It is well known that there are enormous difficulties involved in establishing on a permanent basis the manufacture of dyes on a scale adequate to supply our needs, and that without Government or legislative assistance they might well prove insurmountable; and the action of the Government in proffering such broad-minded and generous support has received, as it deserved, the recognition of all parties.

The German colour industry is probably the most complicated, most highly developed, and most profitable of all her great industries. The capital invested in it is about £12,000,000, and the German exports of dyes and associated products in 1912 were valued at £10,600,000. The organisation, both for production and for marketing and distribution, is wonderfully efficient, and above all the Germans have long realised that in this branch of industry the scientific mind and scientific method must be predominant, not only in the laboratory and in the works, but in the management. The boards of directors of their large works are virtually committees of technical and commercial experts who are in intimate touch with the respective branches of

the works of which they have special knowledge. In a word, the trained man of science has in these works come to his own, and a proper recognition of the necessity of this is vital to the development of the British colour industry.

The reasons for the predominance of Germany in this particular industry have been frequently and variously stated, but it is now generally conceded that there is no lack of highly trained chemists in this country competent to build up a commercially successful enterprise. With regard to other factors, we have, of course, a superabundance of the coal-tar products which form the basis of the manufacture, but the manufacture of certain essential reagents, *e.g.* fuming sulphuric acid, though already existing, will have to be greatly increased.

Government assistance will be required in regard to the provision of cheap alcohol, and the resources and skill of the chemical engineer will be heavily drawn upon to provide the essential apparatus. A great number of chemists will be needed to work out the details of known processes, first on the laboratory scale, and later on a bulk basis, and the well-equipped laboratories and staffs of the universities and larger technical institutions might well be pressed into service for much of the preliminary work. Many chemists will also be required for developing new processes and for other research work, because of no other industry can it be so truly said that stagnation spells failure.

The great complexity of the manufacture of dyestuffs is not due to the use of a large number of raw materials, the direct products from coal tar being only nine or ten. By chemical treatment these are, however, transformed into 250 to 300 different intermediate products which, in their turn, yield some 1200 chemically distinct dyestuffs. In some processes of manufacture high temperatures and pressures are required; in others the temperature must be reduced, and a large refrigerating plant is an essential feature of a colour works.

Surely, then, it is abundantly evident that the technical expert must be the preponderating element in the dye factory, and that he must have a large share in the management and control. The British custom of entrusting the management of large concerns to financiers, commercial magnates, and "men of affairs" has done much to retard the scientific development of our industries, and the adequate representation of the technical expert on the directorate is vital to the success of the new scheme.

Lord Moulton laid down three propositions with regard to the proposed new British dye-manufacturing company. It must be large enough to be able to face severe competition at the end of the war. It must be, and must remain, entirely British, and it must be co-operative; and all these conditions are fulfilled by the scheme put forward. It is proposed that the share capital shall be £3,000,000, and the Government offers to supplement this by a loan of £1,500,000 at 4 per cent. and repayable in twenty-five years. The four and a half millions of capital thus proposed is probably ample to establish and develop an industry which would make us independent of imported products.

The proposals with regard to co-operation are that dyers and others associated with the consumption of the products, e.g. spinners, manufacturers, merchants, textile machinists, etc., should take shares in the new company and thus become interested in its success. This is quite sound and receives general acceptance, but certain suggestions in the prospectus with regard to a *pro rata* subscription appear to be unworkable.

The Government reserves the right of appointing two directors of the company, and it is much to be regretted that the opportunity has not been taken of giving a wise lead in regard to the character of the directorate, by stipulating that the scientific technologist should be adequately represented.

Another feature of the scheme propounded by the committee is that certain existing colour works are to be taken over by the new company to form the nucleus of development. The resources of these works are to be extended as rapidly as possible in order to cope with immediate necessities and prevent an actual famine in dyewares—in fact, large extensions are at the present moment being made.

A point which presents some difficulty in adjustment is the relationship of the new company to existing British dye-producing firms, or such as may be established in the future. It is obviously not desirable to stifle private enterprise by anything in the nature of a monopoly supported by the Government, but the existence of successful German firms which are outside the two great "Interessengemeinschaften," or rings, indicates that the difficulty is more apparent than real. A somewhat cognate matter is the future relationship of the new company to the Swiss firms which are importing to us during the present crisis.

The various criticisms of the Government schemes which

have been offered refer, not to general principles, but in almost all cases to more or less important details. The general outline of the scheme—the establishment, by co-operation of those specially concerned, of a new company with great resources and financially aided by the Government—has received general approval, and the unprecedented step taken by the Government has been applauded by men of all parties, as meeting an industrial crisis in a bold and statesmanlike manner. In response to this, and in recognition of a national emergency, it is the obvious duty of all who are commercially interested to deal with the question from the national rather than from the individual point of view. Support of a scheme for the manufacture in Britain of British-used dyes is, at its lowest estimate, an essential business insurance, and on a higher plane it is helping forward a movement to free our great textile industry from the danger of German domination. Apart altogether from the commercial aspect, there is, therefore, a great obligation of patriotism involved. The scheme put forward—possibly as a *ballon d'essai* as regards details—certainly requires modification, but from it can be elaborated a national and co-operative effort which is bound to succeed. Let us all take as a starting-point of our deliberations that the thing *must be done*, and then the details of how to do it will fall into proper perspective.

Finally, it may be pointed out that incidental advantages of enormous national value will accrue as the result of the successful fruition of this dyeware manufacture scheme. The necessity for dealing with our industries from a national, rather than an individualistic, point of view will be more fully recognised by the Government and by the public. The necessity for the use of scientific method and control of our industries will be strongly emphasised. The claims of patriotism and the value of co-operation in commercial matters will receive fuller consideration. And lastly, the establishment of a powerful company for the manufacture of organic dyestuffs will afford protection to our great industries concerned in the manufacture of inorganic chemicals, an attack on which was beginning to be organised.

Now is our opportunity, and everything is propitious. Patriotism and self-interest are alike clamouring for the establishment of a large dye-manufacturing concern, and the Government offers its support. One essential thing may, however, be overlooked—the new company is foredoomed to failure unless a

scientific rather than a purely commercial spirit permeates the management, and an appeal is made to the Government and to the eminent business men forming the committee who have issued the scheme that in its final form it may include a full recognition of this fundamental point.

## II

### THE GOVERNMENT'S MODIFIED SCHEME

(*Nature*, 25th February 1915, p. 700)

The discussion on the various aspects of the problem of producing in this country an adequate supply of dyestuffs proceeds without intermission. The question has for some time assumed a national aspect and has been the subject of Parliamentary debate or question on at least three occasions. It has also been debated at meetings of the Chambers of Commerce in the chief industrial centres, and people most directly interested have had many opportunities of expressing their opinions at meetings of their various organisations, or at gatherings specially convened for the purpose.

To a great extent the discussions have centred round the adequacy and equity of the commercial proposals involved in the official scheme now before the public. These have received much more general acceptance than those put forward in the first scheme, and it appears probable that the committee has now received promises of support to an amount representing a substantial proportion of the initial capital proposed for the new company.

The members of the committee themselves admit that it is an easy matter to criticise the scheme adversely, and it is obviously impossible to devise a solution of the problem satisfactory to all minds.

If the matter is to be viewed as an ordinary commercial proposition, if questions of free trade or protection are to be taken into account, or if early dividends are to be assured, then any scheme which might be put forward could be shown to be unworthy of support. But whilst criticism on these lines has been plentiful, there has latterly been a rally of support by those taking broader views—a support which has probably been largely induced by a sense of national need, and has certainly been



greatly developed by the action of the Government in offering to endow the research work which is essential to the extent of £100,000. This action has engendered a feeling of confidence that the Government will take any further steps which the future may show to be vital to the success of the British dye-manufacturing industry.

It is to be hoped that the committee in charge of the scheme will shortly be able to announce the results of its inquiries, and that these will show that the great textile trade of the country has responded adequately. In the meantime, the arrangements for carrying out the necessary preliminary chemical work should be proceeded with.

### *A Mobilisation of Chemists*

Speaking in Bradford on 8th February, the present writer advocated immediate action by the Government or the Board of Trade Advisory Committee in the direction of utilising the services of British chemists. There is on one hand a large amount of chemical work to be done before the industry can be greatly developed, and on the other there are a great number of well-staffed and well-equipped laboratories in our universities and technical colleges which might render great service to the industry. To avoid wasteful duplication of work and to co-ordinate the results, it is essential that some organised scheme and allotment of work should be arranged, and it is suggested that a conference of those concerned should be held at an early date to formulate such a scheme. Even if to-morrow the whole of the available chemical force set to work on some organised plan, it would not be any too soon to get the necessary information together for the use of the existing works and the new works when they are started.

The urgency of this action is further shown by a resolution passed by an important meeting held in Manchester on 16th February, which was presided over by Sir Charles Macara. The resolution, which was carried unanimously, stated: "That in the opinion of this meeting the Government would do well to organise immediately the present chemical talent in the country with a view to chemical research being undertaken for, and on behalf of, all manufacturers interested, and that the services of these experts should be available for all desirous of availing themselves thereof."

The adoption of such a plan for bringing the educational institutions more closely into touch with the industries would in all probability mark the beginning of a new era in which both would benefit. The more intimate association of professors of chemistry with chemical industry would introduce into the works that higher ideal and broader scientific spirit upon which successful research and development depend, whilst the schools would benefit by the great incentive of practical reality.

XXIX.: 1915

## THE CHEMICAL INDUSTRIES OF GERMANY

BY PROFESSOR P. FRANKLAND, F.R.S.

[*Abstract*]

(*Nature*, 11th March 1915, p. 47; *Journal of the Society of Chemical Industry*, April 1915, p. 307)

THE interest and importance of the subject at the present time are sufficiently obvious. In outlining some of the origins of chemical industry in Germany, the lecturer pointed out how the royal house of Prussia had been frequently associated with chemical enterprise. The Markgrave John was actually surnamed "the Alchemist"; the Great Elector was a patron of chemistry and provided a laboratory at Potsdam for the celebrated Kunkel, one of the first to discover phosphorus, and who also effected great advances in the manufacture of glass. Frederick the Great established the Royal Berlin porcelain factory, which still occupies some of the original premises. In the same reign also the chemist Marggraf made those classical investigations on the occurrence of sugar in the vegetable kingdom which later led to the foundation of the beet-sugar industry, which was initially subsidised by Frederick William III., the founder of the University of Berlin in 1809. (In 1914, the Berlin University had 12,585 students, and received an annual grant from the State of more than £200,000.)

Great industries have developed out of these early steps. From the discovery of phosphorus came the match industry. The German annual production of matches is £4,600,000; the British production in 1907 amounted to £775,000, whilst the British consumption in 1910 was estimated at £1,300,000. Again, the porcelain and pottery manufacture had attained great dimensions in Germany, the exports in 1912 amounting to

£3,556,000, whilst the glass industry was even on a larger scale, the recent annual exports being more than £7,000,000. Great inconvenience in connection with all scientific work is at present being experienced through the absence of German glass. The important cyanide industry may be said to have taken its origin from the accidental discovery by Diesbach, of Berlin, of Prussian blue in the first decade of the eighteenth century. Germany's annual production of cyanides is now estimated at 10,000 tons (£650,000), or about one-half of the world's production.

The beet-sugar industry exemplifies how agricultural production can be improved by systematic research such as has been bestowed on it by Germany ; thus :—

In 1840	100 lb. of beet yielded	5·9 lb. sugar.
1850	" " "	7·3 "
1870	" " "	8·4 "
1890	" " "	12·5 "
1910	" " "	15·8 "

Again, in

1871	mean yield of beet per hectare of land was	246 quintals.
1910	" " "	300 "

And again, in the economy of manufacture

In 1867	coal used on 100 lb. beet	. . . .	35 lb.
1877	" " "	. . . .	24 "
1890	" " "	. . . .	10 "
1900	" " "	. . . .	7 "

The former supremacy of Great Britain in the manufacture of the common chemicals—sulphuric acid and soda—was referred to and compared with the production of these materials in 1910.

#### PRODUCTION IN TONS, 1910

	Germany.	England.	France.	United States.	World.
Sulphuric acid .	1,250,000	1,000,000	500,000	1,200,000	5,000,000
Soda . . . .	400,000	700,000	200,000	250,000	2,000,000

The substitution of the ammonia-soda for the earlier Le Blanc soda process, and of the contact for the time-honoured leaden chamber process of sulphuric acid manufacture, had no doubt greatly assisted both Germany and America in becoming independent of the British manufacture of these chemicals.

During the past twenty-five years the manufacture of chlorine and caustic soda by the electrolysis of common salt (sodium chloride) has been realised and rapidly extended. This process

is carried out on a very large scale in Germany, where extensive use is made of liquefied chlorine. The production of electrolytic chlorine is attended with the simultaneous evolution of large quantities of hydrogen gas for which uses have been found; thus, for filling the dirigible balloons upon which such hopes of conquest have been based by Germany, whilst in the oxyhydrogen flame it has been employed for welding, for the cutting even of thick iron structures, and for the manufacture of artificial gems. The artificial production of gems—corundum, ruby, sapphire, etc.—was discovered in France by Michaud, Verneuil, and Paquier, and has been greatly taken up by the Elektrochemische Werke at Bitterfeld, in Germany. More than a ton of these gems, which are identical in chemical composition with the natural gems, are said to be annually produced. Other more important uses for hydrogen have been found for the hardening of fats, and still more recently for the synthetic production of ammonia to be presently referred to, and which is an industrial achievement of the first magnitude. Cheaper sources of hydrogen than the electrolytic method have been introduced, and notably that depending on the production of water-gas (consisting of equal volumes of hydrogen and carbon monoxide) from steam and coke at a red heat, the carbon monoxide being subsequently separated from the hydrogen by liquefying it by means of the low-temperature apparatus of Carl von Linde, of Munich.

#### AMMONIA, NITRATES, AND FIXATION OF FREE NITROGEN

As is well known, one of the most important problems at the present time is to provide the world with nitrate when the deposits in Chile shall have been exhausted. The problem is bound up with the still wider one of the fixation of atmospheric nitrogen. This again, as is well known, is now accomplished on a large scale by the production of nitric acid from atmospheric nitrogen and oxygen by means of the electric furnace of Birkeland and Eyde, or by the production of calcium cyanamide by passing atmospheric nitrogen over heated calcium carbide. Both these processes involve the use of the electric furnace, in the former for effecting the union of the nitrogen and oxygen, and in the latter for the preliminary production of the calcium carbide. Abundant water-power being necessary for the economic operation of the above processes, Norway has become their chief centre,

whilst Germany has sought other means of nitrogen-fixation which could be carried on within her own territories. The synthesis of ammonia from hydrogen and atmospheric nitrogen under a pressure of 200 atmospheres and at 500° C. in the presence of a catalyst, has been successfully worked out by Haber in conjunction with the Badische Anilin- und Soda-Fabrik, and a plant capable of yielding 130,000 tons of sulphate of ammonia per annum was to have been ready in 1915. The second step in the German programme was to convert the ammonia into nitric acid by burning it in air in the presence of a catalyst. In this way it is hoped to make Germany independent of foreign countries for the nitrate required in the manufacture of explosives. It is asserted that this independence Germany has actually secured at the present moment.

### EXPLOSIVES

Of the modern high explosives, gun-cotton was discovered by Schoenbein and by Boettger in 1846. The manufacture of nitroglycerine (discovered by Sobrero in Paris in 1847) was first realised by the Swede, Alfred Nobel, in 1862, and it was Nobel who first adapted these powerful explosives for ballistic purposes. Trinitrotoluene, of which so much has been heard recently, was first proposed for filling shells by Haessermann in 1891. It is said to be surpassed, both as regards safety and disruptive effect, by tetranitro-aniline discovered in England by Dr Fluersheim. The great magnitude of the German explosives industry is seen from the following figures :—

	Tons.
Total German production of explosives . . . .	40,000
or about one-tenth of the estimated world production.	
Germany exported in 1908 to the value of . . . .	£1,000,000
1912 „ „ . . . .	3,000,000

### ARTIFICIAL SILK

This remarkable industry, originated by Count Chardonnet in France in 1891, has also been largely developed on German soil. The German production amounts to about 2000 tons annually (£1,200,000) out of a total world production of about 7000 tons. French, German, and British patents have largely contributed to the success of this industry.

## INDUSTRIES DEPENDENT ON SYNTHETIC ORGANIC CHEMISTRY

It is in respect of these industries that the world is learning that Germany holds the undisputed supremacy. It is in Germany alone that manufacturers have been found prepared to embark their capital and undertake industrial enterprises of the first magnitude on the advice of the organic chemist. The success which has been achieved by the German manufacturers of artificial dyestuffs, drugs, and perfumes, and the hegemony which they have secured in this branch of industry, has been the frequent subject of warning by professors of chemistry in this country for upwards of a generation. The seriousness of the situation which has arisen through the neglect of those warnings is seen from the following figures :—

Annual value of dyestuffs used in Britain . . . . .	£2,000,000
"    trade in which these dyes are employed . . . . .	200,000,000
Workmen dependent on this trade, 1,500,000	
Total value of dyestuffs imported (1913) into Britain . . . . .	1,892,055
"    "    "    from Germany . . . . .	1,730,821

Less than one-tenth of the annual value of the dyestuffs consumed in England is produced in this country. Thus, by controlling the dyestuff industry, Germany indirectly holds in her grip the whole of the textile industry.

Much inconvenience has been experienced also in the shortage of artificial drugs and consequent high prices, more especially at the beginning of the war, as even the simplest of these products were almost exclusively made in Germany. The manufacture of some of these is, however, now being successfully carried on in England.

Again, the shortage of organic chemicals required for research purposes, which practically all come from Germany, is occasioning most serious difficulties in our university laboratories.

For the manufacture of dyestuffs and similar synthetic products Germany was formerly largely dependent on England for the raw material—coal-tar. But in this case, again, the ambition of Germany to become in all respects independent and self-contained has led her in recent years to make the most strenuous efforts to recover the maximum amount of coal-tar both from the manufacture of gas and from coke-ovens, which endeavour has been assisted by the enormous growth in her iron and steel industries. Thus in 1897 Germany obtained only

52,000 tons of coal-tar from coke-ovens, whilst in 1908 she obtained no fewer than 632,400 tons from that source, besides 300,000 tons from the manufacture of gas. Thus at the present time the German output of coal-tar about equals, if it does not exceed, that of England.

The German production of artificial perfumes is said to amount to a value of about £2,500,000 annually. In this department of applied chemistry, again, one of the first steps was made by the late Sir William Perkin, by the synthesis in 1868 of coumarin, the much-valued odoriferous principle of woodruff (*Asperula odorata*).

The effect of artificial synthesis on the price of natural perfumes may be gathered from the following examples :—

	Price of 1 kilo.		
	Natural.	Synthetic.	
	£	£	s. d.
Coumarin . . . . .	25	1	5 0
Vanillin . . . . .	50	1	10 0
Heliotropin . . . . .	150	10	0 0

The proposal of the Government to assist the British coal-tar colour industry is being watched with the greatest interest both by manufacturers and chemists. The problem of relieving the immediate shortage during the war must be carefully distinguished from the later problem of securing the independence of the home industry after the war by greatly increasing the British output. The realisation of the latter object will be attended with the greatest possible difficulty. The industry will require "nursing" for a great many years. The undertaking must be possessed of such elasticity that it can ramify into other branches of chemical or other industry whenever advantageous opportunities arise for such departures.

The great magnitude of the German coal-tar colour industry may be gathered from the fact that the two groups into which the principal firms are associated have at the present time a total share capital of about £12,000,000, on which a dividend of about 28 per cent. is paid. In 1912 Germany produced dyestuffs to the value of £12,500,000, of which to the value of £10,000,000 were exported.



The above facts speak for themselves and proclaim in the most convincing manner the stupendous progress which has been made by Germany in the chemical industries during the past forty years. It is equally certain that England, once pre-eminent for chemical manufactures, has not progressed at the same rate and is at the present moment suffering much inconvenience through being so largely dependent on German chemical products of one kind and another. The country is now reaping the harvest of humiliation which it has sown for itself in spite of the warnings repeated *ad nauseam* during a whole generation. The systematic neglect of chemical science and the failure by manufacturers to utilise the services of highly qualified chemists, could only lead to the result that all the industries which are dependent on a profound knowledge of chemistry should tend to disappear from our midst and pass into the hands of those who are prepared, not only to apply new chemical discoveries to industry, but even to prosecute the most varied chemical investigations in the hope of sooner or later making discoveries which shall be of advantage to their commercial undertakings. The mischief caused through the neglect of chemistry by practical men in this country has been so subtle that to a large extent it has remained concealed from the average man of intelligence and from the governmental classes. During the past forty years our country has been accumulating wealth in an altogether unprecedented fashion, so that the loss or restriction of some industries appeared a matter of no importance to political observers taking only a broad and superficial survey of the national resources. The whole of our arrangements have evolved during the past half-century on the assumption that this country would never again be engaged in a European war, whilst still more recently the new democracy has vainly boasted that it could prevent such a war by means of a general strike. The year 1914 has seen the dissolution of many fools' paradises and has given the *coup de grâce* to all these vain imaginings, with the result that we find our vast textile industry in serious peril because the much smaller dyestuff industry has been complacently allowed to slide into the hands of our sagacious and more pains-taking enemies. The same carelessness and want of foresight had even allowed us to become dependent on Germany for some of the most important materials used as explosives, *e.g.* trinitro-toluene, and for many of the most valued drugs required alike by our Army, Navy, and civil population.

The complete breakdown in our supply of fine chemicals, which is the direct outcome of the disregard of the constant warnings emitted by scores of British chemists, has led the Government of the day to intervene and attempt to remedy the intolerable state of affairs which has arisen in connection with the supply of coal-tar colours.

We devoutly hope that success will attend the endeavour to establish the coal-tar colour industry in these Islands on the largest possible scale. Whatever the ultimate scheme adopted may be, I would venture to point out that it must be based on a clear understanding of the following considerations : (1) That the provision of the required chemicals during the continuance of the war is one thing, and that their production on a commercial basis after the cessation of hostilities is quite another matter. (2) It appears to me that in order to provide the needful supply during the war, the only reasonable course is to assist in every possible way those firms which are already making similar or closely allied products so as to enable them to produce their present goods on a larger scale, and as far as practicable to undertake the manufacture of others which are urgently required. The immediate problem will be also greatly facilitated by utilising supplies obtainable from neutral powers, and more especially from Switzerland, which is the only country, other than Germany, in which the manufacture of dyestuffs and similar chemical products has been vigorously prosecuted. (3) As regards the prospects of the home industry after the war, it will require "nursing." I use the term advisedly in order to obviate the employment of another and much more familiar one which is so dear to some politicians and so hated by others ; it will require nursing for a much longer period of time than has hitherto been mentioned. In this connection I would point out that the sum of £10,000 a year for ten years, which it has been proposed to guarantee for research purposes, is absurdly inadequate. (4) If the industry is to prosper it will not only have to manufacture materials already known, but also continually to be introducing new products of its own discovery, as well as constantly to be seeking to produce more economically a great number of auxiliary chemicals required in the manufacturing processes. It is also essential that the undertaking should branch out into the manufacture of other materials as occasion may arise for advantageously utilising by-products. (5) The competition

which the industry will have to suffer from Germany is likely to be much more serious than is generally supposed, because it must be remembered that England only takes, as we have seen, about one-fifth of the total German exports of dyestuffs, so that it would be comparatively easy for German firms specially to reduce the price of the goods sent to England. They have already done this in America when attempts have been made to start a dyestuff industry there. It is particularly significant, and augurs ill for the prospects of this scheme to rehabilitate the coal-tar colour industry, that the latter has failed to flourish anywhere excepting on German soil, and that countries with fiscal systems entirely different from our own have been no more successful in this respect than have we ourselves. (6) It will certainly be necessary that expert chemical knowledge should in the future be much more highly remunerated than it has been in the past, otherwise the supply of able and properly qualified men will not be forthcoming. The flow of men of high-grade intelligence into a profession is determined by the prizes which the profession has to offer, in the form of money and social position. Consider the great stream of able men who are attracted to the English Bar, in which profession the prizes, although limited in number, are of the most substantial kind, with the result that the successful leaders are selected by the fiercest competition in a very wide field. If there is to be a large influx of high intelligence into the chemical profession, it will be necessary that there should be some very different prizes from the paltry bait which is offered at the present time, for the study of chemistry in this country now only draws those men who either have or think they have an overpowering zeal and passion for the science, to which they devote themselves against the advice of their friends. Notwithstanding the absence of material inducements, I venture to say without fear of contradiction that there is more original investigation being prosecuted in this country by chemists than by any other body of British men of science, and this I attribute to the fact that such a large proportion of our number have either been at German Universities or are the pupils of those who have been at these centres of research. Nor are any of us, I am sure, even during this unfortunate crisis, unmindful of the hospitality and the inspiration which we have received in the schools of the enemy. (7) If the proposed undertaking is to succeed, real chemists must be on the directorate,

and in a sufficient proportion to give effect to their views. Many men of science are excellent business men. What does experience teach in the case of flourishing chemical industries which we fortunately still have amongst us? What does not the firm of Messrs Brunner, Mond & Co., for example, owe to the late Dr Ludwig Mond, F.R.S. ? (8) In attempting to establish a commercially successful coal-tar colour company on a large scale in this country, I venture to think that the Government have undertaken a task which they will find to be surrounded with difficulties of quite a different order from those which they have had to encounter in some of their most striking previous legislative acts, such as the provision of salaries for members of Parliament, the granting of old-age pensions, and the establishment of a compulsory system of insurance. These are matters in which if the Government dictate we are obliged to obey ; but the commercial success of an industry which is based upon progressive scientific investigation depends upon factors so subtle and elusive that they cannot be coerced even by a majority of the House of Commons. (9) If the chemical industries are to be rehabilitated in this country, there must be a complete change in the attitude of mind towards science in general, and towards chemical science in particular, amongst the influential classes of the population, and it will certainly not be effected by following the precept "Business as usual," but by pursuing a policy which is the exact opposite of what is implied by that phrase.

XXX.: 1915

## PATENT LAW REFORM

By J. W. GORDON, K.C.

(*Journal of the Royal Society of Arts*, 12th March 1915, p. 356)

(*THE first portion of the paper gives a very interesting summary of the development of technical education in England and in Germany.*)

In the year 1867 all the world was looking admiringly upon the high development and great prosperity of British industry. Just as we to-day speak with respect of the technical educational institutions of America, France, Switzerland, and Germany, so in 1867 those other countries were speaking with the like respect of our widely diffused mechanics' institutes and art schools. Sir Bernhard Samuelson, who was in personal contact with our industrial neighbours while at the same time he was an enterprising industrial captain himself in this country, was by no means satisfied that these developments, which attracted the favourable notice of our neighbours, were sufficient to do justice to ourselves. At great personal trouble and expense he produced a report of which Mr Mundella, the Minister for Education, in 1881 spoke in high praise, as a State document. In 1882 Sir B. Samuelson became the Chairman of the Royal Commission known as the Duke of Devonshire's Commission. In 1897 the same Commission produced a second report, in which the further development of the technical education and institutions of Germany was made the subject of comparison with the past and with our then existing system. The appearance of the second report of the Commission gave rise to an important newspaper discussion which furnished the occasion for a very remarkable utterance by Sir Bernhard Samuelson, in a short letter which appeared in the *Times* of 25th January 1897, and runs as follows :—

"In your leader on the report of my late colleagues on technical progress in Germany, you refer to the fact that the production of dyes from coal tar, in which we have been so completely distanced by the Germans, was originated by Dr Perkin, and, it might be added, by Dr Hofmann, in this country.

"It is not generally known that we lost this manufacture because the trade in England was shut up for fourteen years by a master patent whilst no controlling patent had been sanctioned in Germany, so that anyone could take up the manufacture there; the result being, of course, development abroad in place of stagnation at home.

"At the present time we in this country are handicapped as much as before, but from an opposition (*sic*) of things. The Germans, having taken the lead with their acquired experience and large capital, keep it by patenting their new processes in this country, but carry out their manufacture abroad. So long as they keep our market supplied, which they take care to do, nobody is at liberty to make the patented articles here."

The case to which allusion was made in the last paragraph was an action tried in our own courts in 1883, and brought by the Badische Chemical Factory against Levinstein & Co., a firm of dye manufacturers in Manchester. Seldom has an action of greater practical importance been the subject of proceedings in a court of law.

The German patentees in that case were the inventors of a dyestuff, a chemical body having a definite chemical composition and a specific name. It may be sufficiently identified by speaking of it as a sulpho acid of a coal-tar product yielding red and brown dyes. In respect of the dyestuffs which they were the first to produce, the German patentees obtained a British patent which was unquestionably good. Those dyestuffs, however, were of no appreciable commercial value.

The patent was taken out in 1878, and it was five years later that the action against Levinstein came to trial. The patentees then complained that a very successful red dye which Levinstein manufactured was an infringement of their patent. In the view which the court took of the nature of the patent this claim was upheld, and judgment accordingly was given in their favour. But the circumstances were very singular, and such as to place the court in a difficult position when deciding upon the issue of fact. It was proved that the dye which Levinstein manufactured could

not be produced by the processes which the inventors had described, indeed could not be produced by any process which was known to the inventors. The successful dye, which was taken to answer to the chemical composition of the patented invention, was produced by a secret process, and special arrangements were made for taking the evidence in such a manner that the Levinstein secret was not disclosed except confidentially to the court and its officers. The patentee, therefore, although he was allowed to restrain the second inventor from working his own invention in this country, did not acquire a knowledge of the nature of that invention. Thus the action resulted in a deadlock, and the operation of the patent law in this case was to banish the manufacture of the patented dye from this country altogether. The patentee could not make it because he did not know how, the real inventor could not make it because he was restrained by an injunction of the court. So it happened that by this perverse operation of the patent law a patent, which had been granted with the avowed object of introducing into this country the manufacture of the sulpho-acid dyestuffs, operated to prevent their introduction. In the end the manufacture was carried on in Holland, where the German patentees had been unable to obtain a patent. No statistics have been published from which the value of the dye industry which was thus transferred to Holland can be ascertained, but credible information goes to show that the cloth sent from Manchester to Holland to be dyed with Blackley red represented an industry which, in the aggregate, was worth many millions of pounds, and Sir Bernhard Samuelson's warning is of special importance at a moment when the investment of a large sum of money is in contemplation with the object of establishing an industry similar to that which was so ruthlessly destroyed by legal process in 1883.

Now, in a case like this it is quite impossible to attribute the loss of the industry to any defect in our system of technical education. In 1883 a Patent Act had been passed by which provision was made, among other things, for the remedying of the mischief which this case illustrates. It is not, however, to be supposed that the draftsman of that statute had the facts of the Levinstein case in mind. That, indeed, was impossible. The Act was passed in 1883, and the action was only tried in that year. The consequences of the decision in that action could not possibly have been known until a later date. But although it

had not been illustrated on so large a scale, the mischief was perfectly well known to students of our industrial development in 1883. It is not surprising, therefore, to find that an attempt was made to remedy the mischief.

It has been shown that the operation of the patent law in the *Levinstein* case was to render the use in this country of a valuable invention impossible, and to banish the resulting industry to Holland. It needs no argument to show that that is a complete miscarriage. The object of the patent law is to facilitate the introduction of new manufactures within the realm. Whether we look upon the patent as an instrument of public policy, or as a reward granted to a meritorious inventor, the result from this point of view is the same. The merit of the inventor or the object of the policy, as the case may be, is to secure the advantage of an improvement in manufacture for the benefit of the people of this realm. In law, no less than in policy, the outcome of the *Levinstein* case was absurd and lamentable. How, then, could such a result come about? The answer to that question is that it came about by the operation of the rule which makes an injunction by the court the remedy for an infringement of patent right.

In spite of the stringent provisions of the Statute of Monopolies (1624) the injunction is to-day what it was in the days of Elizabeth and James I., the main support of patent right, and, as the case quoted shows, it has been used in modern times with effects even more disastrous for the industry of this country than in those ancient days, when it aroused the hostility of Lord Coke and the antagonism of a reforming Parliament.

Enough has been already said about the mischievous effect of this particular injunction upon the dyeing trade of Lancashire. But the facts cover a very much larger field than this particular sulpho-acid dye, a field in fact much larger than the field of dyestuffs, a field which is larger even than the whole chemical industry. But we are more immediately concerned with its bearing upon the proposal to establish dye manufacture upon a very extensive scale within this country.

From that point of view the important fact in the *Levinstein* case is, not that the manufacture of a particular dye was prohibited within the realm, but that the way of improvement was closed. The peculiar mischief of this decision was that it made it more advantageous for an inventor who improved upon the



original patent to go to Holland and practise his improved invention as a secret process than to practise it in this country under the provisions of our patent law. To establish such a state of things was obviously cutting at the root of development. A few carefully disposed patents can, under such a system, block the whole development of an industry against all the world except only those privileged people who chance to be the holders of the pioneer patents. It is a matter of no consideration that these pioneer patents themselves may be perfectly worthless for all practical purposes. It is their existence, not their merit, which constitutes the strength of the patentee's position.

This situation was clearly apprehended at a very early date in the history of the chemical industry by our German competitors. A system of blocking patents has been an organised industry with the great German manufacturing chemists at least since the year 1883 ; and when we hear of the large staffs which they keep employed upon research work in their factories, it is well to remember that, over and above those results of this laboratory industry which take effect in improved processes and products, there is a large output of novelties which are improvements only in a legal sense ; the real value of which is that they eventuate in patents of this blocking type which close the avenues of improvement to other inventors.

It is impossible from any available data to ascertain to what extent the British chemical industry has been sapped by means of such mischievous patents, but this system of sapping has been systematically and extensively developed, and it has had an immense success.

In all these cases the cause of our weakness is the injunction. It is to be understood that, according to the practice which prevails to-day, a perpetual injunction is granted as a matter of course to protect a patentee who has successfully established his patent rights against an infringer.

Such being the mischief, we may now turn to consider what are the remedies which Parliament has provided. The earliest attempt was embodied in a section (22) of the Patent Act of 1883, which provided a remedy which has come in recent years to be well known under the style of a compulsory licence.

If this contrivance of a compulsory licence had been effective, it would have met the whole difficulty. It would have prevented

the mischiefs which have arisen, and would probably have placed the patent law of this realm in an entirely sound position. But a very hard fate has pursued the reformers of our patent law. This provision was still-born and never produced its intended effect, a result which was due to faults of draftsmanship.

*(A detailed discussion of the Patent Act of 1883 follows here.)*

The provisions of the Act of 1883 concerning compulsory licences were never tested experimentally, for, although several petitions were lodged and carried through to a conclusion, they were all carried through under such unfavourable conditions that anything more than an unsatisfactory success was rendered impossible. It is not surprising, therefore, that the agitation already referred to for a reform of the Act of 1883 should have gathered head and eventually should have prevailed in Parliament. In 1900 a Departmental Committee was appointed to consider further remedial legislation, and in particular to advise Parliament as to the adoption of the Continental provision of the compulsory working within the realm of patented inventions. The Committee reported against the compulsory working provision, and in favour of a reference of petitions for compulsory licences to the High Court. The report contained also some other suggestions, and in the ensuing year Parliament proceeded to legislate on lines generally indicated by the Committee. Instead, however, of adopting the suggestion that petitions for compulsory licences should go to the High Court, Parliament took the extraordinary course of sending them for consideration to the Privy Council. This expedient did not help matters at all. The division of authority was still as marked and as mischievous as when the petition was sent to a referee, and the practice of the Privy Council tended rather to aggravate than to reduce the costs incidental to the carrying of the petition through. So far the last case was distinctly worse than the first, and in 1907 Parliament proceeded to deal with the matter for a third time.

The Act of 1907 was closely modelled upon the German patent law. Accordingly a new remedy was introduced in the shape of a condition making the working of a patented invention within the realm compulsory, but the nature and measure of the working to be required and the conditions which furnished an excuse or imposed liability upon a patentee were left to be settled by the judges in the administration of the law. It was probably a wise expedient on the part of Parliament to leave these matters

thus in a plastic condition to be moulded and fixed by the action of the judicature. The idea no doubt was that the obligation of compulsory working would, on the one hand, discourage the practice of taking patents for the purpose of blocking an industry, and, on the other hand, would secure the development within the realm of industries which are protected by patent right. The Act has only been in operation for a period of about seven years, and it is too soon perhaps to attempt anything like an estimate upon historical foundations of its possible outcome. It may be pointed out, however, that it has not had very much effect so far upon the chemical industry. To those who have a practical acquaintance with the conditions of the problem this will not be surprising. The complications which it presents in its judicial aspects are enormous. In part they may be illustrated by the facts of the *Levinstein* case which have been described. In such a case as that, for instance, where there was no market for the goods which the patentee could manufacture and a large market for the infringing goods which he did not know how to make, what is the patentee's obligation under the law of compulsory working? Must he manufacture, to satisfy the law, a certain quantity of unmerchable goods, or is he to be held liable to manufacture the improved goods whose production is the infringer's secret? The inherent difficulties are such that nothing would be less surprising than that it should be found in the end to be what it appears to have been in the beginning, an expedient wholly ineffective for any useful purpose.

Such being the situation which has actually arisen, it will be useful to consider the bearing of this situation upon the proposal now made to establish, in competition with the German industry, a self-sufficient industry in this country in the manufacture of dyestuffs. We may take it for granted on this occasion that no insuperable difficulty will arise. So far as research and technical education are concerned there is not likely to be the smallest difficulty about securing, and at once securing, the necessary trained skill.

Let us assume that the works are started and in successful operation. That fact will not make any difference to the subsisting patent rights in this country of which, as is well known, a very large proportion are held by foreigners and others whose interest it is to favour the foreign competition with this domestic industry. Now it is clear, therefore, that there will be a strong

disposition to repeat the *Badische coup* of 1883, and then, adopting the language of the judgment in that case, we may say that notwithstanding "the great knowledge, great skill, and great perseverance" which will be brought to bear in building up these industries, the law will be invoked to say that the processes so developed cannot be used in the production of the colouring matters manufactured because the production of those colouring matters is protected by patent rights. It may at once be admitted that the new institution will be placed in a very different position from that which was occupied by the defendant in the *Badische* and *Levinstein* action. In the present case there is a possibility of applying to the Board of Trade for a compulsory licence, and if it were certain that such a proceeding would succeed it would in substance remove the difficulty. There would still be an important question of procedure to be considered, but that is probably not of great importance. It cannot, however, be taken for granted that an application for a compulsory licence would succeed. The grounds on which such an application can be made are strictly limited and, in fact, very narrow. If the patentee himself takes adequate steps to supply the British market with his patented goods, then, according to the interpretation adopted by the courts of this provision of the statute, no order for a compulsory licence can be made. Now, in the case at least of important goods for which a large and profitable market exists, there seems to be no conceivable reason why the foreign patentee himself should not supply the demand. It is quite true that he may be called upon to conduct his manufacture within the realm, but he cannot be called upon, as matters stand, to grant a licence to the new institution. He may prefer to remain an active and privileged competitor with the new institution, and so, although with diminished power of mischief, may still succeed in casting his blight upon the undertaking. The carrying on of the new industry under these conditions would seem likely to be extremely fruitful of litigation, but by no means equally assured of success; for if it were possible to close any particular manufacture down as the result of a successful patent action, then it cannot be denied that nobody at the present moment is in a position to say what precise field of industry will in the end remain open to the proposed institution. This is the difficulty with which the promoters are faced. The research work of the laboratories of which we have lately heard so much

has resulted in an immense and extremely intricate network of patents designed to protect, by their entanglement, the whole field of chemical industry, which the Germans have made their own. Hitherto these entrenched patents have afforded very efficient protection—partly, no doubt, because the defence of the British industry has been left to the uncoordinated efforts of British manufacturers, who have been attacked one at a time and beaten in detail. It does not, of course, follow that it would be equally successful against a fully organised effort to create a British industry ; but, on the other hand, nobody can be justified in asserting, as our patent law is understood and administered at the present time, that such a large and organised institution would have any better chance than the resolute manufacturer, like the Levinstein Company in 1883, of making an effective stand against the overwhelming brute force of a judicial injunction.

*(An analysis of defects in the existing patent law, and suggestions for their removal, follow here.)*

Patent right is a privilege of such a character that it would not be impaired for the purposes of beneficent operation by being subject to a larger discretion in the exercise of the power of suspension reserved to the Crown than is provided for in the Patent Act. The objects of the grant are threefold :—

1. The common good and benefit to the realm.
2. Reward and recompense for the industry, trouble, and charges of the patentee.
3. The encouragement of other inventors in such laudable and commendable labours as may tend to the good use and service of the realm.

Now it is obvious, and may be taken to be generally admitted, that such an absolutely unrestricted power of exclusive manufacture as was conceded in the Badische and Levinstein case tends directly, not to promote, but to subvert the first of these objects. It tends also to produce that just cause of grievance which it was one of the declared objects of the Crown to avoid in connection with the grant. Hence it may be said, with confidence, that the relief by injunction which was granted in the Levinstein case is subversive of the objects of the patent grant itself. The practical question, therefore, is not whether the power to restrain infringement by injunction shall be wholly uncontrolled, but to what extent it should be controlled. The obvious answer to this question is that it ought to be controlled

to such an extent as to secure all the objects of the grant ; including the avoidance of any just cause of grievance. An answer in those terms, however, is not very instructive, because the practical difficulty is to discover those rules of practice which will attain the end. One inference may, however, with confidence be drawn even from this extremely indefinite statement of the principle, and it is this : The injunction ought not to go as mere matter of course, and without consideration of the circumstances of the case. A court, when granting an injunction, ought to satisfy itself that the injunction will not cause the inconveniences which followed in the *Badische* case, and, therefore, something more than mere infringement ought to be established to justify a court in granting a perpetual injunction.

The general principle with regard to injunctions was thus stated by Lord Brougham :—

“The principle which, as I humbly conceive, ought, generally speaking, to be the guide of the court and to limit its discretion in granting injunctions, at least where no very special circumstances occur, is that only such restraint shall be imposed as may suffice to stop the mischief complained of.”—*Blackmore v. The Glamorganshire Canal Navigation*, 1 Mylne and Keen, 185.

Coming to a narrower and, for our present purpose, more pointed statement of the principle, we have it formulated by Lord Lindley in the following terms :—

“The very first principle of injunction law is that *prima facie* you do not obtain injunctions to restrain actionable wrongs for which damages are the proper remedy.”—*London and Blackwall Ry. v. Cross*, Law Rep., 31 Chanc. Div., p. 369.

The careful observation of this salutary rule would obviously preclude such mischievous results as we are now discussing, and with such authority as it is possible to cite for the rule one may without presumption speak of the existing and mischievous practice as being a lapse from the sound doctrine of the English law.

Let it be supposed, then, that by some means, either by a voluntary recurrence on the part of the courts to Lord Brougham's rule, or, failing that, by legislation, we were to arrive at a satisfactory settlement of this practice, is there any reason to think that the system would work badly and would unfairly prejudice the rights of a patentee ? For the purpose of discussing this question, I will assume that recourse is had

to Parliament, and that an enactment has been put upon the statute book which goes in one particular beyond the older practice of the Court of Chancery. I will assume, that is to say, that the enactment provides in effect :—

(1) That no perpetual injunction shall in any case be granted to restrain infringement of a patent right, but only an injunction to stand until further order ;

(2) That no injunction shall be granted to restrain infringement of a patent right unless it is proved to the satisfaction of the court that the mischievous result to the patentee from the infringement proved is such that he cannot obtain adequate relief in respect thereof from the defendant charged with the infringement.

What would be the result upon patent rights of such a modification of the existing practice of the courts ?

(1) It would at once put an end to the blackmailing type of patent action. In recent years a practice has grown up of bringing patent actions against perfectly innocent infringers who have no sufficient interest in the dispute to make an effective defence. Now it is clear that if no injunction could be granted, but only damages in a case of that sort, the patentee would find that type of action a very unprofitable investment.

(2) Again, in a case such as the *Badische* action, it is clear that the patentees would have been wholly unable to destroy the British industry which they set themselves to attack. In fact, it is probable that the result of that action would in such a case have been more satisfactory to them as well as to the defendant company than in fact it was. If they could not have obtained an injunction they would have had to be content with damages ; and although it may be presumed that in the circumstances of that case the damages would have been small, they still would have amounted to something.

The proposal to establish a large manufacturing industry under the existing conditions of the aniline-dye manufacture is one which raises not only the commercial questions of capitalisation and organisation, but also, in a very pressing form, the comparatively dormant question of a reform of the patent law. The comparative backwardness of our manufacture in this line, easily as it is explained by those who allege the indolence, supineness, and inaptitude for this class of industry of the British manufacturer, can nevertheless be fully explained

only when the pitfalls of our patent law are also taken into account. There is no doubt that both in 1852 and in 1883 substantial improvements were introduced into the administration of our patent law. That the Act of 1907 made for improvement is open to much question. It complicated our system by the introduction of incongruous elements, chiefly from the German patent code, but it left untouched the mischiefs which destroyed the British manufacture of aniline dyes, and laid us open to misunderstanding and reprisal in foreign countries without securing any countervailing advantage for our own manufactures and manufacturers.



XXXI.: 1915

## THE SUPPLY OF DYEWARES

BY PROFESSOR R. MELDOLA, D.Sc., LL.D., F.R.S.

(Abstract of Presidential Address to the Institute of Chemistry,  
1st March 1915)

EARLY in August last year, as appeared from a question raised in the House of Commons, it was foreseen that difficulties might arise in this country, and that certain industries—especially those connected with textiles—might be seriously affected through the stoppage of supplies of chemical products, more particularly dyestuffs, for which we were dependent to a preponderating extent upon German factories.

I may be pardoned on the present occasion if I venture to recall a warning which I sounded nearly thirty years ago. As far back as 1886, I foresaw that the coal-tar colour industry as conducted by us was doomed to decadence in this country.<sup>1</sup> Systematic inquiries made among the consumers revealed the fact that even at that time 90 per cent. of the dyestuffs then in use here were of foreign manufacture. The voluminous newspaper correspondence which has been going on in connection with this subject all over the country during the last few months shows that, in military parlance, no lost ground has been regained—before the outbreak of the war we were still importing nine-tenths of our colouring matters from Germany and Switzerland. Since 1886, on every suitable occasion, I have been endeavouring to instil into the public mind the lesson that the development of this industry abroad has been due to the recognition and utilisation by manufacturers of the results of chemical research. To me, therefore, the crisis threatening our textile industries is no matter for surprise—it appears simply as a relationship of

<sup>1</sup> See Meldola, *Jour. Soc. Arts*, 1886. See p. 121, *ante*.

effect to cause. It is generally supposed that the prophet who, justified by events, is enabled to say "I told you so," is privileged to regard himself with the greatest complacency. In the present case, the only feeling I am able to express is one of humiliation : it is absolutely painful that under the stress of circumstances our weakness should have been laid bare to all the nations—a weakness for which there can be found no justification in the plea that no alarm had been raised or that the supply of chemical talent in this country was inadequate.

The President of the Board of Trade appointed early in August a committee for the purpose of advising the Government with respect to the means of meeting the national requirements, with the Lord Chancellor, Viscount Haldane, as chairman. From this main committee there was subsequently formed a sub-committee for dealing especially with the manufacture of dyestuffs, under the chairmanship of Lord Moulton, whose extensive experience in matters connected with this branch of applied chemistry is well known.

It is now public knowledge that a scheme formulated by the Government in consultation with a committee representative of the great dye-using organisations was put forward at the close of last year, and after full discussion by those immediately concerned was finally referred back for modification. This is not the occasion for entering into a detailed analysis of the various grounds on which the scheme was considered unsatisfactory, but the Government has determined—as I think, wisely—not to allow the project to fall through, and has now launched a new scheme which differs from the first in certain important particulars. Whether this new scheme will materialise remains to be seen : so far, all that can be said is that a considerable number of the dye-consuming companies appear to be favourably disposed towards it. It would be out of place here to attempt to explain or to criticise the scheme as it stands, but I want it to be clearly understood, as there has been much public misapprehension on this point, that for neither of these schemes is the Board of Trade Advisory Committee or the Dyestuffs Sub-Committee in any way responsible. The grounds on which it was considered that public action was imperatively called for were set forth most clearly in an address delivered by Lord Moulton at Manchester, on 8th December of last year,<sup>1</sup> and in

<sup>1</sup> See p. 351, *ante*.

that address he stated explicitly that he only held himself responsible for the advice that the Government should take action, but not for the particular shape or form which that action should assume. Out of the present situation, therefore, there arise certain general considerations which the chemical profession will do well to take note of, and for this reason I will venture to direct your attention to some of them.

In the first place, stating the case baldly, and in the broadest possible terms, the principle is adopted that there should be established a company in which the consumers should be the chief shareholders, and which the Government should subsidise by advancing capital at a certain rate of interest to the extent of £1,000,000. It is unnecessary to go into details, but it will be seen that the scheme is in a way a co-operative one and that, for the first time, we have a distinct proposal in this country for the establishment of a State-aided industry. It is beyond our province to discuss this proposal in its economic or political bearings. In view of the great interests at stake, the policy appears to me to be a sound one, as was admitted by both political parties when the proposal was mentioned in the House of Commons last November by the President of the Board of Trade (*Times* report, 28th November 1914). What concerns us most as representatives of the chemical profession is that our aspect of this great industry should be kept well to the fore in the present scheme, or in any other scheme that may hereafter be put forward.

In the next place, I take it for granted that we all desire to see the restoration of the coal-tar colour industry to this country, and, be it noted, not only restored, but permanently retained after the war. Now, the discussions of the Government schemes in various parts of the country by dye-consuming organisations, Chambers of Commerce, and so forth, have all centred round political or economic questions; that which is to us the vital principle, viz. adequate chemical control, has been subordinated or left out of consideration altogether. It is the old, old story—we wrangle over the question as to the method by which the industry shall be established and maintained here, whether by Free Trade or Protection, or Subvention or by any other device, and we leave out of consideration the question whether a few years hence there will be anything in the way of dyestuffs worth protecting; whether there will be a sufficient basis of material

products left for the politicians and economists and business people to wrangle over. It is not a purely business problem which the Government has undertaken to solve ; it is primarily a chemical problem. It is not even a business problem in the ordinary trade sense, because the main object is at first to supply our own wants, and the chief consumers are to be the chief producers. The question of business in the sense of export trade is at present remote.

The conditions which have to be met if we wish to see this country once more the home of the colour industry may be well known to us here, but are certainly imperfectly understood by the public. Even those most concerned—those who are invited to subscribe the capital—appear in most cases to have an idea that all that is necessary is to find the money, secure the Government aid, appoint a board of business directors, and lo ! the industry will forthwith spring into existence ready to cope with all emergencies. Now, what are the facts of the case ? About five hundred different dyestuffs of definite compositions have been given to tinctorial industry as the products of chemical research. Of these, a certain number only can be and are being made in this country, the total output of our factories being at present inadequate for the requirements of our textile industries. The first step to be taken, therefore, is to enlarge and develop our existing factories so that the dyes which can be made here should be turned out in larger quantities. This necessity has, of course, been provided for in the Government scheme, and so far so good. Moreover, if the extension of the existing factories still leaves us with insufficient supplies, new factories must be erected and equipped. That also is provided for in the scheme ; but if we want to establish the industry here permanently we must look beyond all this—where shall we be left after the war ? We shall be in possession of processes for making a certain number of dyes, and the supply of this particular set of products may possibly be sufficient for the particular purposes for which they are required. Let us label these provisionally “staple products.” But there will still be an outstanding number—probably a majority—of other products which we have never yet made here, and for the working out of these processes no combination of “business” talent is of the slightest value. I repeat, it is not a business question, but a chemical question, and it is by chemical research alone that

our colour industry can be saved in the long run. Consider the leeway that we have to make up. The German colour industry has been built up by the utilisation of the results of research carried on in the factories and universities and technical schools for a period of over forty years! To suppose that we can retrieve our position after forty years of neglect by starting a company the directorate of which is to consist solely of business people is simply ludicrous. It was against this principle that I ventured to raise my voice in the *Times* of 20th January last, and I am extremely glad to find that not only the chemical and technical worlds, but the large and representative body of dye users and producers which form the Dyewares Supply Enquiry Committee of the Society of Dyers and Colourists, fully endorse this view and have forwarded to the Board of Trade a resolution, passed at Manchester last month, in support thereof. A meeting of the Federation of the Light Leather Trades held at the Leathersellers' Hall on 22nd February passed a similar resolution. It is satisfactory to learn that there are at any rate some of the dye-consuming organisations which have grasped the situation scientifically. To imagine that a dyer, however skilful he may be, is, by virtue of his occupation, necessarily competent to direct the affairs of a company which is concerned with the manufacture of the dyes which he uses, is about as sensible as the assumption that a person who can tell the time by his watch is thereby qualified to undertake the direction of a factory for the construction of chronometers.

One feature of the new scheme which the chemical profession will view with favour is the distinct recognition of research as a necessity for the development of the industry. The Government "will, for ten years, grant not more than £100,000 for experimental and laboratory work." That, although an inadequate endowment, is certainly a concession which marks an advance in official opinion for which we are grateful. It will be for the satirist of the future to point out that it required a European war of unparalleled magnitude to bring about this official recognition of the bearing of science upon industry. It would be but a truism to state here the purposes for which research is required; the question we have to raise is—Who is to direct this research? A directorate of purely business people would certainly be incompetent; a board composed of dye users could do no more than indicate what dyestuffs were needed. True, it

is proposed that the company should take powers to secure the assistance of a committee of experts, but this appears to me to be simply a reversion to that policy of "drift" which I have for so long been struggling to overthrow. The experts are, as usual in this country, subordinated; their assistance is to be invoked at the discretion of a board the members of which can have no real knowledge of the conditions necessary for producing the materials they require now—still less would they be competent to point out dangers ahead. The "staple products" upon which they are asked to stake their capital may a few years hence be superseded by the products of subsequent discovery. The policy of attempting to run a highly specialised and rapidly developing branch of organic chemical industry by a company of business people, with expert assistance when required, is fatal if we want to establish the industry permanently here. The group of industries which have arisen from the products of the tar-still are not going to remain stagnant after the war, and it is scientific guidance and not mere assistance that will keep them alive. It is the expert, and the expert only, who can foresee the course of development, who can keep in touch with the progress of research, and who can direct with intelligence the campaign against our competitors. If such scientific direction is withheld, all schemes are sooner or later bound to end in failure.

XXXII.: 1915

## THE POSITION OF THE ORGANIC CHEMICAL INDUSTRY

BY PROFESSOR W. H. PERKIN, F.R.S.

(Presidential Address delivered to the Chemical Society, 25th March 1915 :  
*Journal of the Chemical Society*, 1915, p. 557)

THE subject which I have chosen for my address on this occasion must always be regarded as of the highest importance, not only to this Society, but also to the country at large, because of its intimate connection with the prosperity of so many of our largest and most successful industries. It is a subject which has been discussed over and over again at scientific societies, in scientific journals, and particularly in the newspapers by chemists, manufacturers, politicians, and the general public. In his valuable presidential address to this Society in 1907, entitled "The Position and Prospects of Chemical Research in Great Britain," Professor Meldola had much to say about the bearing of research on the position of industry; and in 1909 the same writer discussed very fully the question of the value of education and research in connection with applied chemistry in his presidential address to the Society of Chemical Industry. It would therefore seem scarcely necessary that I should take up your time by bringing these matters to your notice again. I do not propose, however, to apologise, partly because I am of the opinion that a summary of the position of the organic chemical industry in as few words as possible will not be out of place and may be useful, but more particularly because, in spite of the large amount of literature bearing on the subject, I feel convinced that the causes of the decadence of this industry in this country are still imperfectly understood.

The seriousness of the position is readily grasped when it is borne in mind that the value of the colouring matters consumed in this country is at least £2,000,000 per annum, and that more than 90 per cent. of this quantity comes from Germany; and, when it is remembered that these dyes are essential to textile industries representing at least £200,000,000 per annum, and employing more than 1,500,000 workers, it is easy to see to what an alarming extent these great industries are in the grip and power of the Germans. There are, of course, many other industries which depend on colouring matters for their existence, such as, for example, the wallpaper, the printing, and paint industries, to all of which lakes and pigments are absolutely essential, and of late years almost the whole of these have been imported from Germany. Again, the enormous quantities of organic chemicals required for photographic purposes—such as, for example, pyrogalllic acid, hydroquinone, metol, and many other similar developers,—the natural and artificial products employed in such huge quantities in the manufacture of scents and perfumes, the synthetical and other drugs which have in some ways revolutionised medical science, and also many of the more important disinfectants, have been almost exclusively made in Germany. We may add to this list the vast trade in fine chemicals, for here we are again completely outclassed, since there are no firms in this country which can compete with Kahlbaum, Merck, Schering, de Haen, and a host of others either in the range or the purity of their products, and it has long been our habit to import almost all our organic fine chemicals from Germany. It may indeed be said that Germany has no competitor worth considering in the whole domain of organic chemical industry. That we should have allowed trades of such magnitude to pass almost completely into the hands of a foreign nation seems incredible, and, as the inevitable result, we are face to face with the serious position that, the foreign supply having stopped, stocks are rapidly vanishing and prices are rising to such an impossible level that the progress of several of our industries is greatly hampered. Indigo, perhaps the most essential of all dyes, is manufactured entirely by the great German colour works, and the stock in this country a few weeks ago was so low that the price rose to at least ten times what it was before the war; the same thing is happening in other cases, and many dyes cannot be obtained at any price. Obviously we



must take warning, and not allow, in the future, our textile and so many other similar industries to be controlled in this way by the foreigner, and to be in danger of being brought to a standstill.

How are we to explain the fact that we have allowed some of our most important industries to get into this critical condition, and what do we propose to do to remedy this state of things and prevent any recurrence in the future? No one doubts for a moment that the wonderful opportunity of establishing a great national industry, due to the discovery of the aniline dyes in this country, has been allowed to escape us, and various reasons have been put forward to explain the loss of the colour industry. There can be no doubt that a good many different causes have been at work. One of the main reasons for our position is that we as a nation, and our manufacturers in particular, have failed to understand the extreme complexity of the scientific basis of organic chemical industry, and have concluded that this industry could be carried on much in the same way as the manufacture of sulphuric acid, caustic soda, and other heavy chemicals. The manufacturer has always been unwilling to acknowledge that neglect of science in his works is the real cause of his failure to retain the colour industry in this country, and has therefore put forward all sorts of other reasons to explain his want of success.

Thus it has been urged repeatedly that our patent laws were greatly to blame, and that these laws were such that an English patent was no protection, and that so soon as anything new had been discovered in this country the Germans at once set to work to manufacture it.

Even if this were true—and there may be some truth in it—it does not explain why the Germans were able to obtain their raw material as they did in this country, to transport it to Germany, and then to send the dye over here, and at the same time to make a handsome profit out of the transaction. Again, it has been urged that the obstacles to the use of pure alcohol which existed at the end of the last century played a great part in bringing about the decadence of the coal-tar colour industry in this country. Possibly there has been some hardship in special cases, but a Departmental Committee of the Board of Trade took evidence from a large number of experts in this country and in Germany, and issued a report on "Industrial Alcohol" in 1905, and the Committee arrived at the conclusion that, as a statement

of historical fact, the assertion that the coal-tar industry has been lost to this country on account of obstacles to the use of pure alcohol is devoid of substantial foundation.<sup>1</sup> Of late years the restrictions on the use of duty-free alcohol have been so relaxed and the denaturants which may be employed are of such a wide range, including as they do the actual articles to be manufactured,<sup>2</sup> that there is probably at the present time less difficulty put in the way of the manufacturer here than is the case in Germany.

It is quite obvious that other reasons than those I have just mentioned must be found to account for the gradual transference of the coal-tar industry to Germany. The decadence of this industry and its gradual transference to Germany may be said to have begun during the period 1870-75. It was in 1874 that the works of Perkin & Sons at Greenford Green was sold to the firm of Brooke, Simpson & Spiller, and these works were then in the most prosperous condition, and much in advance of anything that existed in Germany.

One reason for the sale was my father's natural dislike to an industrial career, and his desire to devote himself entirely to pure chemistry. There was, however, a much more weighty consideration which played the really important part in his decision to dispose of the works.

It was recognised—and, as the subsequent history of the coal-tar industry has shown, correctly recognised—that the works could not be carried on successfully in competition with the rising industry in Germany unless a number of first-rate chemists could be obtained and employed in developing the existing processes, and more particularly in the all-important work of making new discoveries. I remember quite well that inquiries were made at many of the British universities in the hope of discovering young men trained in the methods of organic chemistry, but in vain. There cannot be any doubt that the manufacturer of organic colouring matters during the critical years 1870-80 was, owing to the neglect of organic chemistry by our universities, placed in a very difficult and practically impossible position. At that time organic chemistry was not recognised by the older universities,

<sup>1</sup> See p. 228, *ante*.

<sup>2</sup> For example, the manufacturer of pure ether may denature the alcohol he uses by the addition of a little sulphuric acid, and, in the case of diethyl-aniline, this substance or aniline may be used as the denaturant, and so on.

and the newer universities, which have since done so much for the progress of science, had not come into existence. It is surely remarkable that the study of so important a subject as organic chemistry should not only have been practically ignored by our universities in the past, but that even at the present day it does not flourish in the way it does in almost every university and technical school in Germany.

This seems to me the more remarkable when it is borne in mind that all problems connected with life, either in the animal or vegetable kingdom, are essentially problems which depend on, and are largely controlled by, organic chemistry, and it is therefore clear that little progress can be made towards the solution of such problems until the processes of organic chemistry are clearly understood. Quite apart, therefore, from its industrial aspect, organic chemistry must, from the purely scientific point of view, always be regarded as a branch of science of the very highest interest and importance.

If the record of our universities is examined, it is at once obvious that many of these famous places, and more particularly the universities of Oxford and Cambridge and the Scottish universities, contributed practically nothing to the advancement of organic chemistry during the latter part of the last century, and their output of research in this subject is still far less than it ought to be. It is difficult to understand why our universities should so persistently hold aloof from progress, and should so often entirely fail to gauge the importance of leading the way in new developments, on which, after all, in many cases the welfare of the country depends. How very different is the picture exhibited by the attitude of the German universities towards organic chemistry during the critical period I have mentioned!

So soon as the importance of organic chemistry became apparent, great teachers, such as Liebig and Wöhler, Kekulé and Baeyer, founded schools specially devoted to the subject, and they and their pupils then began to publish that wonderful series of classical investigations which laid the foundations on which the superstructure has since been raised.

The value of the example of these great teachers and of the system of research which they had initiated soon became generally appreciated by the universities in Germany, and every effort was made, by the establishment of laboratories supported by adequate grants from the various States, to help forward the new move-

ment. The step which, in my opinion, did more than anything else to bring about the wonderful development of organic chemistry in Germany was the provision that research must be an essential part in the training of every German student of chemistry.

In almost every direction, and to a far greater extent than has been the case in any other country, Germany has recognised the value of the closest possible contact between the industries and the universities. In Germany the majority of the Professors and Privatdocenten are in close touch with the large factories, and spend part of their time in solving technical problems which they either devise themselves or which may be submitted to them by the manufacturer.

I have it on the authority of several of the best-known directors of German works that the atmosphere of the university laboratory is much more suitable for discovery than that of the works, and that, as a fact, many of the most valuable discoveries which subsequently proved to be of the highest technical importance have been made in university laboratories and transferred to the works as the result of the intimate connection I have just described. Moreover, when it is remembered that the important dyes, malachite green, the phthaleins, artificial alizarin, and indigo, and the pharmaceutical products antifebrin and antipyrine, to mention only a very few cases, were discovered in university chemical laboratories, it is quite clear that there is much truth in the statement of the works directors. Close association of the universities with the industries does not exist to any extent in this country, and is one of the things we have to aim at in the future, however distasteful this may appear to some of our academic circles. Systems of training and methods of teaching which may have been useful centuries ago, but have become antiquated, must, in these days of acute competition, give place to methods that are more in accordance with existing requirements and the practice of other nations; otherwise we are bound to fall behind in the race.

It must, I take it, be assumed that the aim of the university is to acquire the best scientific ability for its professoriate and teaching staff, and therefore the home of the best scientific research talent must always be the university laboratory; it is therefore quite clear that close association between these laboratories and the works must be of great advantage to industry. Such a

connection cannot fail to be of great value also to the university, for it must result in the manufacturer taking a keen interest in the welfare of the department with which he is associated; he will willingly provide material from his works for teaching and research, and subscribe liberally to the resources of the department, and no scientific laboratory—chemical, physical, or engineering—can do good work unless it is liberally supplied with material and funds.

It has often been suggested to me that a professor who is engaged in solving problems of a technical nature will have no time for other scientific research work, and that, since results of technical value must often be kept secret and may never be published, the reputation of his department will suffer. Experience shows, however, that such is not the case, for there is little, if any, diminution in the output of research work in pure science from the German laboratories as the result of this system.

We must, I think, agree that one of the main reasons for the rise and development of the German chemical works is the appreciation on the part of the manufacturer of the value of science in connection with industry, and the recognition of the great importance of a close alliance between the works and the research laboratories of the universities and leading technical institutions of the country.

My view is that contact with the research department of a large works must always be stimulating; problems are encountered, many of them of great scientific interest, which would never suggest themselves in strictly academic circumstances; and as one of the results, the tendency, which is always present under existing university conditions, for the professor to become an academic fossil and unproductive is postponed. Again, we are all aware how difficult it often is to find suitable research subjects for the budding chemists under our charge, and contact with the research departments of a flourishing works cannot fail to suggest subjects for investigation which are eminently suitable to occupy the attention of young men, many of whom will ultimately take up technical work. I look forward to the time when the scientific staffs of our universities and technical schools will not only be available for industrial research, but will be encouraged by those in authority to undertake such work; for I am quite certain, and indeed it is very generally admitted, that the association

of the best academical talent in the country with the technical laboratories of the works can only be of the highest mutual benefit.

After all, this kind of thing is quite common in the case of the engineering departments of our universities and technical schools ; and if the system works well in the case of engineering, there is surely no reason why it should not be equally successful in the case of chemistry.

Our competitors have, from time to time, given their opinion as to the reasons for the transference of the organic chemical industry from this country to Germany, and, as such views cannot fail to be instructive, it will not be out of place if I quote one such utterance. On the occasion of the jubilee of the discovery of mauve, in 1905, Dr Duisberg, one of the best-known directors of the colour works of Bayer & Co., in Elberfeld, went fully into this question, and I propose to read a few extracts from his remarks which have a special bearing on this matter. Dr Duisberg said : " You inquire further, and wish to know how it is that the German soil, in which the coal-tar colour industry has grown so powerful, varies from English soil ; what particular conditions were there which had been so advantageous for its fructification ; whether it was not eventually possible to produce artificially the same conditions also in England, and that here also in the land of its birth those rich and golden fruits could not be gathered, the harvest of which is reaped by Germany year by year. I do not believe in such acclimatisation in England, at least for the present. No other industry requires so much uniformity of thought and action, science and practice, as organic chemistry and the organic chemical industry.

" In Germany, not only has chemical science developed to a considerable extent, but at the same time the technique of organic chemistry has flourished. Both have stimulated and vitalised each other, and both have supported each other. Such was not the case in England. Although the Englishman is in general practical, he is wanting in that peculiar quality which we Germans are remarkable for—that is, not perseverance, but patience and the power of waiting for success. For all the Englishman does he expects soon to be compensated in hard cash."

Continuing, Dr Duisberg used the following words, which are particularly interesting in view of the present crisis : " But

you will say, when the problems have been solved, and when the patents have run out and the manufacture is free to everyone, 'Why should not the English and foreign works decide to cope with the German firms and compete against them?'

"In my opinion this would be futile, and would be of no avail. Even in Germany, where, as we have seen, the conditions are the most favourable, it would now be scarcely possible, or at least be a singular coincidence if a manufacturer, although possessed of energy and capital, should succeed in building up a new firm in the colour line so as successfully to compete against the existing powerful works. Whereas, therefore, the conditions in England for many industries, such as for the mining industry, for spinning and weaving, not forgetting inorganic chemistry, are far more advantageous than in Germany, the latter country has the natural privilege in the organic chemical industry, and other nations should not envy her in this, but leave it to her."

It is because we have acted in the manner recommended by Dr Duisberg, and have left the coal-tar colour industry to Germany, that we find ourselves in the present grave and serious position.

Views similar to those of Dr Duisberg have been expressed in many quarters, and Lord Moulton, speaking at the Royal Society of Arts on 3rd December of last year, gives an example which is also very much to the point.<sup>1</sup> "I read," he said, "the other day with bitter feelings the address of one of the ablest industrial chemists in the world—the head of one of the German chemical industries—who, talking about this very subject, said: 'England talks not only of holding her own in the war, but of beating us in the chemical industry. She cannot do it, because the nation is incapable of the moral effort of taking up such an industry, which implies study, concentration, patience, and fixing the eye on distant consequences, and not merely on the monetary result.'" Lord Moulton himself puts the matter in this way: "Some fifty years ago organic chemistry opened up a domain of industrial wealth that he could only compare to that opened up by the discovery of steam power. He had been able to come to but one conclusion—that, either from being too well off, or from sluggishness of intellect, or from the fact that the capital of the country had passed into the hands of people who were unwilling either to learn or to think, England had abstained almost entirely

<sup>1</sup> See p. 347, *ante*.

from an attempt to reap the rich harvest open to the industrial world by the advance of organic chemistry." In his address delivered in the Town Hall, Manchester, on 8th December 1914, Lord Moulton said : "Gentlemen, we have to look the truth in the face. It (the loss of the coal-tar colour industry) was for no other reason than that the English dislike study. The Englishman is excellent in making the best of the means at his disposal, but he is almost hopeless in one thing. He will not prepare himself by intellectual work for the task that he has to do. Now there is the cause and, so far as is material, the sole cause of the German supremacy. Is that a cause which must permanently operate? The answer is, of course, 'No.' But it is for us to reform ourselves ; otherwise no relief can come."<sup>1</sup>

I have ventured to read these short extracts because they contain the gist of the matter, and because I cannot think of any words which might describe the position better.

If, then, we accept the enormous technical importance of organic chemistry, and recognise, as Lord Moulton puts it, that the industry is so vast that it can only be compared with that opened up by the discovery of steam power, and if we decide that we are not going to allow—as Dr Duisberg suggests that we should—all this wealth and prosperity to pass entirely into the hands of a foreign country, what course must our manufacturers adopt in order to get a share of this? I have already said, and everyone will agree, that they must, in the first place, make up their minds so to conduct their works that research is going on unceasingly ; no works can possibly flourish which is content to manufacture only well-known colours, and it is only by the discovery of new colours and other products that manufacturers can hope to get a satisfactory return on their capital. The manufacturer must therefore see that his laboratories are properly equipped, and well supplied with research chemists of ability, who have had a sound scientific training, and also some experience in the methods of research. All this, however, will avail little unless he has a scientific leader in his works who is able to direct the investigations of his young staff in the right channels.

Students of mine who have entered chemical works have frequently complained to me that there is no one over them qualified to direct their investigations, and that original work

<sup>1</sup> See p. 351, *ante*.



seems to be considered of secondary importance, and only to be indulged in when there is nothing else in the works to occupy the attention of the chemist.

So far as I am aware, there is not a single colour works in this country which has a really brilliant scientific head—by which I mean a chemist of wide scientific experience, and with the knowledge and ability to direct research ; and this is a very serious state of things, and quite incompatible with chemical efficiency.

I have long thought that the want of an able scientific head is one of the most obvious reasons why our colour works are in such an unsatisfactory condition. The success of a business based on science must often be essentially the work of a single brilliant scientific man, just as the success of a great school rests with the headmaster, and the reputation of a university laboratory depends on the ability of the professor.

If a works is fortunate enough to have the services of a distinguished scientific man, capable of initiating and carrying out original investigations, and who will not only be constantly making discoveries himself, but be able at the same time so to influence his young staff that they will follow in his footsteps, the success of such a works can never be in doubt. I am afraid, however, that it will be a long time before we can hope that our manufacturers will give up their old-fashioned rule-of-thumb methods and fully grasp the truth of this vital matter.

My experience of the manufacturer in this country is that he is usually merely a commercial person who does not like the expert, and especially the idea of giving the expert a prominent position in the control of his works. Possibly the reason in many cases is ignorance of the value of science, but more probably it is due to the fact that, being ignorant of science himself, he feels that if the expert is given too much prominence he must either study himself in order to understand the expert or leave the essential control of the business in his hands. Both these courses are distasteful to the ordinary commercial member of a board of directors ; the expert is therefore relegated to the background, and the business comes to grief.

It would seem to be scarcely necessary to point out that, if a chemical works is to be successful, the first essential is that it must be under chemical control, and that every department must be in the hands of an expert ; the board of directors may then

be a mixed board, provided that steps are taken to ensure that chemical opinion is largely represented on it. The recognition of the soundness of this principle is one of the main reasons for the success of the German works.

Anyone who has had the opportunity of visiting the principal German colour works, as I have, cannot fail to have noticed that chemical control is everywhere; the heads of departments are always chemists, and the board of management invariably includes a large proportion of the abler chemical experts employed in the works. Not only do German business men understand that the control of a chemical works must be in the hands of the chemist, but they are also careful to remunerate their chemists liberally and to give them a share in any new development they may initiate, with the result that many of their leading chemists are in receipt of salaries quite unheard of in this country.

When we ask the question whether we can adopt methods of a similar kind in this country we find ourselves at once face to face with very grave difficulties. Let us assume that the necessity for the chemical control of a chemical works is conceded, as conceded it must be, and that it is clearly understood that the next step is the discovery of improvements in every direction, such as the invention of dyes better than those already known, and the economical development of essential existing processes, then the first thing to be done will be for our universities to set to work to educate a supply of organic research chemists who will be able to undertake this work. This will mean that organic chemistry will have to flourish to a much greater extent than it does now, because the supply of organic research chemists available under ordinary conditions is a very small one, and scarcely sufficient to meet even the moderate demand which exists at the present time.

If the effort gradually to develop—it is not a question of immediately establishing—a thriving organic chemical industry in this country is to be seriously taken in hand, and not to be merely talked about, and if the requisite capital is forthcoming, it is obvious that what will be required before everything else will be a really able chemical staff, and there should, therefore, be a great opening in the near future for young organic chemists of ability. It is unfortunate from this point of view that many, probably the large majority, of our young chemists are not immediately available, since most of them are at present engaged

in military service, and therefore the evolution of an efficient chemical staff will be no easy matter. A small beginning may have to be made, but, if the manufacturer will continually bear in mind that chemical efficiency must always be the basis of all his calculations, there is no reason to doubt that success will come in the end, even though it may, and probably will, be very slow at first.

Soon after the outbreak of the war, the critical position brought about by the shortage of the dyes which are vital to both the cotton and wool trades, and the impossibility of importing further supplies from abroad, called for immediate attention. Urgent representations from dyers and calico-printers and others engaged in trades which require large supplies of dyes, forced the Government to see that something must be done, and done as quickly as possible, to find a solution for the extraordinary situation that had arisen. A Board of Trade Committee was therefore appointed on 25th August, with the Lord High Chancellor (Viscount Haldane) as chairman,<sup>1</sup> with instructions to consider the best means of obtaining for the use of British industry sufficient supplies of chemical products, and, after hearing the evidence of many of the more important producers and consumers, a small committee, of which Professors Meldola and Green and I were members, was charged with the task of sifting the mass of evidence which had come forward from all quarters.

The chairman of this sub-committee—Lord Moulton—devoted a great amount of his time and energy and experience of German industrial conditions to the task of interviewing representatives of the industries which were affected by the stoppage of supplies from Germany, and, as the result of the report of the sub-committee to the larger body, a meeting of representatives of industrial firms and associations was held on 10th December at the Board of Trade, when the following resolution was passed unanimously: "That this meeting approves in principle of a national effort being made by the trade to increase the British

<sup>1</sup> The other members of the committee were Mr John Anderson, Dr George Thomas Beilby, F.R.S., Prof. James Johnston Dobbie, F.R.S., Mr David Howard, Mr Ivan Levinstein, Prof. Raphael Meldola, F.R.S., Mr Max Muspratt, Prof. William Henry Perkin, F.R.S., Mr Milton S. Sharp, Sir Arthur J. Tedder, Mr Joseph Turner, and Mr Thomas Tyrer, with Mr Frank Gossling, B.Sc., as secretary. Prof. Arthur George Green, M.Sc., was subsequently added to the committee.

supply of synthetic colours, and welcomes the assistance of His Majesty's Government for that purpose." A committee<sup>1</sup> was appointed, and shortly afterwards recommended a scheme which involved the formation of a joint-stock company, having for its object the manufacture and supply of synthetic colours. Subsequently the Government announced that they were prepared to assist such an effort in the following way: "If a limited Company were formed on co-operative lines with a share capital of £3,000,000, the Government agree to advance to such Company £1,500,000, bearing interest at the rate of 4 per cent. per annum, and secured as a first charge on the assets and undertaking of the Company, and to be repayable in twenty-five years." The important proviso was, however, made that "the interest on the advance and a sinking fund for the repayment are to be payable only out of the net profits of the Company, but are to be cumulative." When this scheme was made public its reception was not cordial, and the application for shares fell far short of what had evidently been expected by its promoters. In explanation of this it should, in the first place, be quite clearly pointed out that neither the Board of Trade Committee nor the sub-committee had anything whatever to do with the preparation of the scheme, and it is certainly extraordinary that a committee consisting entirely of business men, and which did not include a single chemical expert, should have been entrusted with the formulation of a scheme for the founding and developing of a chemical industry.<sup>2</sup>

Had a chemical expert been present I venture to think that such a scheme would never have been placed before the public. It is stated in the memorandum of agreement attached to the scheme that the Company had been incorporated for the purpose, among other things, of manufacturing and selling dyes, colours, and other chemical substances, which, previously to the war, were exclusively or principally manufactured in Germany, and no mention is made of what ought to be the main object of such a Company, namely, the employment of a large staff of research

<sup>1</sup> The committee appointed was Messrs Lennox Lee (Calico-Printers' Association), Milton S. Sharp (Bradford Dyers' Association), H. W. Christie (United Turkey-Red Company), Chas. Diamond (English Sewing-Cotton Company), G. Marchetti (John Crossley & Sons), and R. D. Pullar (J. Pullar & Sons).

<sup>2</sup> Compare Prof. Meldola's admirable letter in the *Times* of 20th January.

chemists under leaders of ability for the purpose of making new discoveries in every possible direction.

It cannot be too strongly emphasised that it is not merely a question of producing the dyes which are required during the war; any company which is formed must be established in so strong a position that it can expect to deal successfully with the keen competition which will be waged with the greatest severity by the Germans after the war.

The promoters of the scheme do not appear to have appreciated the difficulties of the situation, and obviously think that the manufacture of dyes in this country which previous to the war had been invented and produced in Germany is a matter which can quite easily be managed.

It seems to be imagined in many quarters that, in order to manufacture a dye which had previously been made in Germany, all that is necessary is to follow the directions given in the patent dealing with that particular dye. No greater mistake could possibly be made. It is common knowledge that German manufacturers have for many years devoted large sums to the establishment of an efficient staff of patent experts, whose business it is so to word a patent that, whilst it satisfies the requirements of the patent laws of the various countries in which it is taken out, only gives such information as is absolutely necessary, and contains no indication of the process which is used in the actual manufacture. In many cases patents are devised which are of no practical value, and are merely intended to mislead and throw competitors on the wrong scent.<sup>1</sup> The discovery of the most efficient method of working patented processes is therefore often a matter of great experimental difficulty, and may require many months of research. Any new Company started with the object of manufacturing dyes which previous to the war had been made exclusively in Germany must therefore be prepared to employ a large staff of research chemists for a long period without any prospect of return in the way of dividends.

Further, it must always be remembered that the Germans have many years' start of the new Company, and have accumulated such vast experience of methods of manufacture, and more particularly of the recovery and economical use of by-products, that they are able to sell at a profit at very low prices. What

<sup>1</sup> This point is well dealt with by Prof. Jocelyn Thorpe, F.R.S., in a letter to the *Times* of 2nd February.

the new Company has to face is, therefore, in the first place, the problem of working out methods of manufacture and the utilisation of by-products until they have arrived at the same state of efficiency as the Germans, and that, it seems to me, may be a matter of years. While this is being done, the new Company must also be busily engaged in training a large body of research chemists under the supervision of capable scientific leaders, so that the works may develop in as many new directions as possible, because the Company can only hope for permanent success if it pursues a policy of discovery and invention. Another point has also to be borne in mind, and that is that the Germans supply dyes and other products, not only to this country, but to practically all the other nations, and, in the event of a new Company being formed on such large lines that it might prove to be a serious competitor, a German works could well afford to sell at cost price or at a loss in this country and make its profits in other lands until the new Company had been ruined. Lastly, if we are to be allowed to make dyes, etc., during the war according to patents belonging to the Germans, what is to happen after the war? Will the Company be still allowed to use these patented processes, or will the patents again become the sole property of the Germans, and be workable in this country only on the payment of royalties or licences? This matter has, no doubt, been carefully considered by the law advisers of the Government, but, so far as I know, no authoritative statement has been issued which makes this situation clear.<sup>1</sup>

<sup>1</sup> Mr Runciman made the following reference to this important point in Parliament on 23rd February last:—

“The success of the concern would depend largely on the way in which the German patents were administered. The Act passed last autumn as an emergency measure provided that the operators of German patents in this country should have a full chance of conducting them under licence, and it was the intention of the Government not to cripple this Company when the war was over, but to give them every opportunity of making the most of German patents. They would leave over for discussion as between Germany and this country the payment of royalty in respect of these patents. There were English patents in Germany on which he hoped a royalty was being paid there. We should hand over these royalties if Germany would bargain fairly with us. But the operating of these patents which would be undertaken by the new Company would proceed after the war was over, without interruption and without hindrance.”

If this statement means that, besides the arduous task of competing with the well-established German works, the new Company may also have to pay royalties or licences to those works, then it is obvious that the difficulties of the situation will be greatly accentuated.

Although it is a matter of so much congratulation that the Government, which in past years has paid practically no attention to science and the application of science to industry, should, at last, have recognised the necessity for intervening and in no uncertain fashion, I have been forced to the conclusion, largely for the reasons which I have just stated, that the Company founded on the lines of this first Government scheme could not be expected to be successful in achieving the object which we all have so much at heart, namely, the recovery and development of the organic chemical industry in this country. Since the application for shares in the proposed Company was quite insufficient, the Government withdrew the scheme, and substituted for it an amended proposal, which is certainly in some respects an improvement.<sup>1</sup> The new proposal is to form a Company with a share capital of only £2,000,000, towards which the Government will make a loan for twenty-five years, corresponding with the amount of the share capital raised, and up to a total of £1,000,000.

In addition, and with the desire to promote research, the Government have undertaken for a period of ten years to make a grant to the Company, for the purposes of experimental and laboratory work, up to an amount not exceeding in the aggregate £100,000.

This amended proposal is another proof of the determination of the Government to meet the criticisms which were raised against the first scheme in a generous spirit, and to do all it possibly can to assist the efforts of the manufacturers in this country to place the organic chemical industry on a firm basis. If, then, I make certain criticisms of the new proposal, it must be clearly understood that I do not do so in any spirit of hostility to the scheme, but rather in the hope that the adoption of some modifications in the proposals may make the scheme workable and more likely of success. In the first place I hold that the scheme must be considered in the light of the criticisms which I have just advanced in connection with the first Government

<sup>1</sup> The members of the enlarged Committee which is responsible for the second scheme are Sir A. F. Firth, Bart., Sir Frank Hollins, Bart, Sir Mark Oldroyd, Mr H. W. Christie, Mr J. Clarkson, Mr Charles Diamond, Mr Kenneth Lee, Mr G. Marchetti, and Mr R. D. Pullar; and, in spite of Prof. Meldola's letter and other letters to the Press, again did not include expert chemical opinion.

plan, and I hope that these points will be clearly handled in any detailed statement of this or any subsequent scheme.

There are, however, other matters which call for comment. The grant for scientific research may be welcomed as a satisfactory addition to the old proposal, mainly because it shows that the Committee of users of dyes have at last found out that research is necessary if the new Company is to be a success. My own feeling, however, is that the Company ought to provide for research out of its ordinary capital as a matter of course, and should not require a special subsidy for this purpose.

A much better plan, I venture to think, would be to employ this grant to subsidise the research laboratories of those universities and technical schools which are willing to specialise in organic chemistry, and are prepared to train a certain number of research students with the definite view of their subsequently entering the service of the new Company. Supposing the new Company were to adopt the view which I have urged in this address, that closer connection between the universities and the industries is most desirable, and were to work in conjunction with the staffs of some of the leading organic schools, it is quite obvious that the knowledge of the needs of the works which would result from this connection would enable the staff to supply research students of exactly the type required by the works. Such research students would have been trained under the best scientific supervision which the country can provide, and at the same time they would enter the works with a considerable knowledge of the application of organic chemistry to technical operations, and be in a position to tackle with success research problems connected with new discoveries and new developments in the works. The plan of training research students under these conditions is, as I have already pointed out, the one which has long been adopted with such extraordinary success in Germany, and the large subsidies which the various States place at the disposal of their universities allow of the purchase of expensive apparatus and appliances which are outside the inadequate resources of most of the university laboratories of this country.

With regard to the kind of works it is proposed to organise for the manufacture of dyestuffs, etc., which previous to the war had been made in Germany, it would be well carefully to consider



the policy which the Germans have adopted with so much success in the matter of the construction and arrangement of their works. I think that one of the things which must strike a visitor to a great German works more perhaps than any other is the order and cleanliness which reigns everywhere, and the obvious care which is taken that every manufacturing operation shall be efficient in every detail. This order and cleanliness is not confined to the section of the works which deals with organic products; the same state of things is to be observed in every part, as, for example, in the case of the large plants which deal with the manufacture of sulphuric acid, nitric acid, and other inorganic products. Perhaps the idea which is conveyed most vividly by works such as these, all of which are concerned with the manufacture of a very large number of products of widely different character, is that they are, after all, merely laboratories on a larger scale.

A very different impression is got by an inspection of many of the colour works in this country, and it seems to me very doubtful policy to suggest the possibility of the acquisition of works of this kind, which are obviously not efficient, and could only be made so by pulling down and re-building. It may be said that the most efficient only will be taken over, but selection will be found most difficult, because, if the new Company proves a success, great pressure will be exerted by existing works in order to enter the charmed circle, and the argument of unfair competition will be used for all it is worth, and will be very difficult to deal with. Again, it is most important not to lose sight of the fact that the experience of the Germans is all in favour of building up very large works, and against spreading manufacturing operations over small works situated in different parts of the country.

The reason for this is obvious. In the manufacture of any substance, by-products are almost always produced which must either be recovered or used in the manufacture of other saleable products; otherwise serious loss is inevitable. It is exactly in this respect that the Germans are so efficient, and the wonderful organisation which enables them to dovetail one process into another is one of the reasons why the comparatively small works in this country find it impossible to compete with them even in the manufacture of such simple substances as salicylic acid or  $\beta$ -naphthol. In order that by-products may be used to the best

advantage it is obviously essential that all these dovetailing operations must be carried out on the same site, so that it may not be necessary to transport the by-products from one works to another, an operation which could not fail to entail loss. Probably the best course for the new Company is either greatly to enlarge the works of Messrs Read Holliday & Sons, or, if it is difficult to find space for this purpose in Huddersfield, to take steps to acquire a suitable site and erect and equip works thereon, a plan which is mentioned in the explanatory statement as one of the objects of the new Company.

Let us suppose that, in the near future, a practically new works is built on a large scale, and with all the most modern appliances, and that the control of the whole works and of the different departments is placed in the hands of efficient chemical leaders with adequate staffs of chemists under their charge, and that the Company has also large and well-equipped research laboratories busily engaged in discovering new developments and improvements on existing processes ; what prospect has such a works of competing successfully with the existing German organisations and of obtaining a fair share of the organic chemical industry ?

In answering this important question it must again be emphasised that the German works with which the new Company must compete are enormous organisations controlling almost unlimited resources and in a most flourishing condition.

The Farbwerke, vormals Meister, Lucius & Brüning, in Höchst, employs, for example, 350 chemists, 150 engineers and technical experts, 600 clerks, and about 10,000 workmen. The probability of successfully competing with several organisations of this kind, grouped, as they are, in combines in order the more readily to be able to crush competitors and secure the monopoly of the industry, also depends, no doubt, to a great extent on the condition of the German chemical industries after the war. If we suppose that the German companies will continue to work with the same efficiency as before, or will rapidly regain that efficiency, I am inclined to think that we must be prepared to face the certainty that some years must elapse before we can compete successfully against organisations which have taken years to develop and bring to perfection.

Failure to develop on research lines is scarcely conceivable if the works is in charge of a highly trained chemical staff, but,

on the other hand, if it gets into the power of the business man who wants an immediate return for his outlay, is not willing to wait for results, and fails to appreciate the importance of scientific control, then no tariff can avert disaster. I am sure we shall all watch the course of events with the greatest interest, and hope that the new venture may have a large measure of success, and bring back to this country at least a tithe of the prosperity which attaches to the organic chemical industry.



## INDEX OF NAMES

- Abel, F. A., 59, 75, 144, 158.  
 Allhusen, C., 317.  
 Anderson, 51, 52, 53, 91, 236.  
 Anderson, J., 419.  
 Arkwright, 284.  
 Armstrong, H. E., 69, 191, 192, 194, 221, 222.  
  
 Babbage, 284.  
 Badische Anilin- und Soda-Fabrik, 74, 85, 94, 97, 119, 136, 190, 196, 198, 199, 202, 205, 207, 208, 210, 219, 220, 247, 248, 255, 257, 272, 301, 308, 312, 320, 326, 327, 365, 368, 382, 390.  
 Baeyer, A., 50, 53, 74, 95, 97, 98, 122, 123, 200, 204, 205, 207, 263, 264, 265, 272, 315, 324, 411.  
 Bardy, 173, 174.  
 Barlow, T., 148.  
 Barnes, W. C., & Co., 135.  
 Bayer, F., & Co., 198, 210, 224, 225, 414.  
 Beaconsfield, Lord, 190.  
 Beale, 241.  
 Béchamp, 9, 77, 153, 238.  
 Beilby, G. T., 419.  
 Beilstein, 169.  
 Berlin Aniline Co., 198, 301.  
 Bernthsens, A., 102, 131, 193, 224, 325.  
 Berry, A. E., 331.  
 Berthelot, 51, 52.  
 Berzelius, 315.  
 Bessemer, H., 284.  
 Besthorn, 127, 129.  
 Bethels Tar Works, 146.  
 Bindschedler & Busch, 365, 366.  
 Bindschedler, H., 366, 367.  
 Birkeland, 381.  
 Black, J., & Co., 78, 134.  
 Bloxam, A. G., 269, 279.  
 Boettger, 382.  
 Böttiger, 192.  
 Bowrey, J. J., 145.  
 Boyle, R., 284.  
  
 Bradford Dyers' Association, 197.  
 Brandenburg, 63.  
 Bretonnière, 194, 265.  
 British Alizarin Co., 135, 229, 290, 311, 312.  
 British Cotton and Wool Dyers' Association, 197.  
 Brooke, Simpson & Spiller, 64, 126, 198, 237, 250, 303, 410.  
 Brougham, Lord, 398.  
 Brown, J. T., 145.  
 Brunck, H., 204, 219, 221, 324, 326.  
 Brunner, J. T., 63.  
 Brunner, Mond & Co., 388.  
 Bunsen, R., 146.  
 Burt, Bolton & Heywood, 56, 117, 250.  
 Burwell, 219.  
  
 Cahours, 85, 147.  
 Cain, J. C., 243, 278, 294, 297.  
 Calvert, C., 33.  
 Caro, H., 12, 52, 58, 63, 74, 86, 89, 91, 95, 98, 99, 115, 122, 123, 125, 130, 136, 148, 154, 168, 170, 178, 184, 206, 242, 243, 246, 247, 248, 249, 253, 255, 257, 262, 263, 264, 271, 301, 303, 316, 324.  
 Cartwright, 284.  
 Cassal, C. E., 333.  
 Cassella, L., & Co., 196, 198.  
 Chapman, A. C., 330.  
 Chapman, E. T., 61.  
 Chapman, Messel & Co., 250, 255.  
 Chapman, S., 190.  
 Chapoteaut, 163.  
 Chardonnet, Count, 382.  
 Chemische Fabrik Griesheim-Elektron, 214.  
 Cherpin, 29, 171.  
 Christie, H. W., 420, 423.  
 Church, A. H., 33, 35, 99, 147, 150.  
 Clarkson, J., 423.  
 Claus, 129.  
 Claus & Rée, 198.

Clayton Aniline Co., 198.

Cliff, 146.

Clowes, F., 145.

Coblentz, 242.

Coke, Lord, 392.

Coleman, J. B., 301.

Colin, 48, 53.

Collas, 111.

Coupier, 122.

Cox Bros., 133.

Crace-Calvert, 254.

Croissant, 194, 265.

Crookes, W., 145.

Crum, Walter, & Co, 134.

Dale, J., 12, 52, 81, 99, 110, 154, 170,  
242, 301.

Dalmonach Print Works, 155.

Dalton, 284, 315.

Darwin, F., 284.

Davy, H., 284, 315.

Davy, J., 89.

Dawson, Dan, & Co., 301.

Deacon, 214.

Deering, W. H., 145.

De Laire, 82, 84, 122, 159, 161, 163, 243,  
253.

De la Rue, 158.

Dépouilly, P. E., 37, 241.

Dewar, J., 118, 129, 138, 222, 284.

Diamond, C., 420, 423.

Diesbach, 380.

Divers, E., 145.

Dobbie, J. J., 330, 419.

Döbereiner, 29.

Doebner, O., 63, 85, 262.

Dower, 254.

Dreaper, W. P., 279.

Drewsen, W., 207, 264.

Duisberg, C., 282, 289, 292, 294, 325, 414,  
415, 416.

Dumas, A., 53, 91, 142, 146, 164, 236, 315.

Duprey, F., 174.

Dusart, 178.

Emmerling, 205.

Engler, 205.

English Sewing Cotton Co., 197.

Ewer & Pick, 131.

Eyde, 381.

Faraday, M., 5, 47, 53, 79, 109, 110, 123,  
141, 186, 235, 284.

Farbenfabriken Elberfeld (see F. Bayer  
& Co.).

Farbwerke Hoechst (see Meister, Lucius  
& Brüning).

Feilmann, E., 279.

Fichte, 346.

Field, F., 32.

Filehne, 118, 119.

Firth, A. F., 423.

Fischer, E., 60, 85, 86, 119, 125, 193, 262,  
315, 320, 321, 324, 367, 370.

Fischer, O., 60, 84, 85, 86, 118, 125, 126,  
127, 129, 262, 265, 324, 367.

Fluerschein, 382.

Forster, M. O., 348.

Foster, H. A., 310.

Franc Bros., 241.

Frankland, P., 379.

Friswell, R. J., 60, 69, 138.

Fritsche, 4, 142, 187.

Gallik, 97.

Garden, 142, 235.

Gardner, W. M., 314, 371.

Gay-Lussac, 315.

Gessert Frères, 57, 255.

Geyger, A., 170, 175.

Gilliard, Monnet & Cartier, 207.

Girard, C. H., 82, 84, 122, 159, 161, 171,  
243, 253.

Girard and De Laire, 21, 22, 163.

Glaser, 325.

Gordon, J. W., 389.

Gossage, W., 317.

Gossling, F., 419.

Graebe, C., 46, 50, 52, 53, 56, 57, 63, 69,  
91, 93, 111, 122, 130, 177, 178,  
179, 183, 205, 245, 246, 247, 248,  
250, 262, 271, 302, 324.

Graham, C., 70, 284.

Grässler, F., 122.

Green, A. G., 189, 294, 323, 331, 419.

Greenford Green Works (see Perkin  
& Sons).

Grey, M., 40, 155.

Griess, P., 65, 69, 99, 115, 148, 167, 168,  
170, 254, 271, 301, 324.

Grimaux, 85.

Guinon, Marnas & Bonnet, 35, 80, 83,  
154.

Guyot, 242.

Haber, 320, 382.

Haen, de, 408.

Haessermann, 382.

Haldane, Lord, 402, 419.

Hall, T., 144, 145.

Hanhart, 42.

- Harrmann, 120.  
 Harvey, A., & Son, 133.  
 Henderson, 222, 340.  
 Hepp, E., 193, 265.  
 Heumann, K., 210, 211, 272.  
 Heys, Z., & Sons, 134.  
 Hickson, E., 132, 313.  
 Higgin, 49.  
 Hobrecker, 172.  
 Hoff, R., 178.  
 Hofmann, A. W., 4, 6, 17, 20, 21, 23, 25,  
     26, 27, 44, 45, 80, 81, 86, 100, 108,  
     110, 126, 130, 142, 143, 145, 156,  
     158, 159, 160, 162, 164, 166, 167,  
     169, 170, 171, 172, 174, 175, 176,  
     177, 186, 187, 201, 211, 235, 236,  
     242, 246, 253, 254, 262, 278, 300,  
     301, 302, 316, 321, 324, 390.  
 Hollins, F., 423.  
 Holzmann, 167.  
 Hoogewerff, 211.  
 Howard, D., 419.  
 Huxley, T. H., 284.  
  
 Jacobson, E., 176.  
 Julius, P., 170.  
  
 Kahlbaum, 408.  
 Kalle & Co., 208.  
 Kay, 242.  
 Kehrman, 193.  
 Keisser, J., 170.  
 Keith, T., & Sons, 78, 152, 240, 300.  
 Kekulé, 50, 51, 53, 178, 185, 261, 262,  
     268, 322, 324, 411.  
 Kelvin, Lord, 284.  
 Kern, A., 89.  
 Kirkham, 241.  
 Knietsch, R., 213, 215.  
 Knorr, L., 119.  
 Koch, J. J., 94, 249.  
 Koechlin, H., 117, 118, 123.  
 Kolbe, 34, 83.  
 Kopp, E., 28, 164, 165.  
 Körner, G., 129.  
 Kostanecki, 193.  
 Kühlberg, 169.  
  
 Laubenheimer, 325.  
 Laurent, 37, 51, 53, 65, 91, 142, 146, 236.  
 Lauth, C., 29, 61, 84, 85, 171, 172, 241,  
     244, 260, 262, 264.  
 Le Bel, 315.  
 Le Blanc, 380.  
 Leckie & MacGregor, 133.  
 Lee, K., 423.  
  
 Lee, L., 420.  
 Lefèvre, 195.  
 Leibius, 167.  
 Leigh, J., 110.  
 Leonhardt, A., & Co., 198.  
 Levinstein, H., 220.  
 Levinstein, I., 117, 135, 200, 203, 275.  
 Levinstein Ltd., 198, 390, 419.  
 Liebermann, C., 46, 50, 52, 53, 56, 57, 91,  
     93, 111, 122, 177, 178, 183, 193,  
     205, 245, 246, 247, 248, 250, 271,  
     302, 324.  
 Liebig, 29, 109, 110, 315, 411.  
 Liggins, 140.  
 Lightfoot, J., 254.  
 Limpricht, 85.  
 Linde, C., 381.  
 Lowe, 254.  
 Luynes, de, 24.  
  
 Macara, C. W., 288, 377.  
 M'Kendrick, 118.  
 M'Leod, 162.  
 Mansfield, C. B., 6, 111, 123, 142, 158,  
     187, 235, 236, 237, 242.  
 Manson & Henry, 133.  
 Marchetti, G., 420, 423.  
 Martius, 35, 117, 169, 174, 253, 301.  
 Maule, 253.  
 Maw, H. W., 350.  
 Medlock, H., 18, 82, 121, 124, 157, 158,  
     243, 253, 301.  
 Meister, Lucius & Brüning, 68, 126, 136,  
     198, 205, 208, 308, 312, 365, 368,  
     370, 426.  
 Meldola, R., 64, 65, 68, 70, 121, 140,  
     188, 191, 219, 220, 227, 228, 233,  
     234, 257, 259, 284, 294, 322, 323,  
     401, 406, 419, 420, 423.  
 Mène, 99.  
 Merck, E., 408.  
 Messel, R., 190, 255, 348, 350.  
 Michaud, 381.  
 Michler, 89, 90.  
 Miller & Co., 153, 236.  
 Mitchell, W. A., 135.  
 Mitscherlich, E., 7, 65, 77, 109, 110, 111,  
     142, 187, 315.  
 Mond, L., 388.  
 Monnet and Drury, 159.  
 Mortimer, 144.  
 Moulton, Lord, 345, 347, 351, 371, 402,  
     415, 416, 419.  
 Müller, H., 21, 34, 248.  
 Mundella, 389.  
 Musprat, 142.  
 Musprat, M., 419.

- Natanson, 17, 159.  
 Newlands, J. A., 145.  
 Newton, J., & Son, 132.  
 Nicholson, E. C., 21, 24, 64, 82, 86, 99,  
     121, 124, 126, 157, 158, 160, 161,  
     163, 187, 201, 237, 238, 253, 279,  
     301.  
 Nietzki, R., 80, 81, 194, 204.  
 Nobel, A., 382.  
  
 Ogilvie, F. G., 349.  
 Oldham, G. W., & Co., 132.  
 Oldroyd, M., 423.  
 Ormandy, W. R., 335.  
 Orr-Ewing, John, & Co., 134.  
  
 Page, F. J. M., 145.  
 Paquier, 381.  
 Peachey, 315.  
 Pedler, A., 145.  
 Pélilot, 110.  
 Perkin, F. M., 221, 298, 321, 336.  
 Perkin, T. D., 150, 243.  
 Perkin, W. H., 1, 46, 52, 54, 69, 75, 111,  
     118, 120, 121, 124, 125, 136, 141,  
     145, 201, 232, 233, 234, 236, 237,  
     238, 239, 240, 241, 242, 243, 244,  
     246, 247, 248, 249, 250, 251, 252,  
     254, 255, 257, 259, 260, 265, 269,  
     270, 284, 294, 298, 301, 302, 316,  
     321, 384, 390.  
 Perkin, W. H., Jun., 407, 419.  
 Perkin & Sons, 152, 229, 237, 238, 239,  
     240, 243, 250, 251, 253, 254, 260,  
     300, 301, 303, 410.  
 Persoz, J., 24, 34, 35.  
 Phillips, C., 242.  
 Poirrier & Chapat, 28, 61, 84, 115, 173,  
     260.  
 Pope, W. J., 315.  
 Price, A. P., 82, 242.  
 Price, D., 157, 158, 301.  
 Priestley, 284.  
 Pullar, R., 39, 124, 132, 152, 154, 234,  
     240, 241, 298.  
 Pullar, R., & Son, 150, 152, 236, 240,  
     241, 298.  
 Pullar, R. D., 420, 423.  
  
 Ramsay, W., 284, 328.  
 Rawson, C., 221.  
 Read Holliday & Sons, 193, 243, 301,  
     426.  
 Reichenbach, 176.  
 Reid, W. F., 332, 349.  
  
 Renard Frères, 17, 156, 159, 270, 316.  
 Ripley, E., & Son, 132.  
 Roberts, A., 349.  
 Roberts, Dale & Co., 253, 301.  
 Robiquet, 48, 53.  
 Roemer, 93, 183.  
 Roscoe, H. E., 46, 71, 106, 365.  
 Roussin, Z., 115, 118, 169.  
 Royle, T., 135.  
 Rudolph, C., 126.  
 Runciman, W., 422.  
 Runge, F., 4, 15, 34, 79, 142, 186, 235,  
     236.  
  
 Salvétat, 24.  
 Samuelson, B., 389.  
 Sapper, E., 213.  
 Schering, 408.  
 Scheurer-Kestner, 241.  
 Schiendl, 169.  
 Schimmel & Co., 325.  
 Schmitt, R., 34, 83.  
 Schoenbein, 382.  
 Schorlemmer, 52, 81, 254.  
 Schultz, A., 40, 155, 163, 240.  
 Schultz, G., 286.  
 Schunck, E., 48, 49, 53, 91, 93, 183.  
 Seidel, P., 215.  
 Sharp, M. S., 419, 420.  
 Simon-Carvès, 108.  
 Simpson, Maule & Nicholson, 77, 82,  
     122, 126, 157, 158, 161, 237, 238,  
     242, 243, 253, 301, 303.  
 Singer, I., 280, 294.  
 Skraup, 119.  
 Smiles, 215.  
 Smith, 242, 301.  
 Sobrero, 382.  
 Société des Usines du Rhône (see  
     Gilliard, Monnet & Cartier).  
 Spiller, J., 69, 145.  
 Spiller, W., 237, 238, 243.  
 Starck, J. D., 242, 255, 256.  
 St Claire Deville, 148.  
 Stephenson, R., 284.  
 Stevenson, J., & Co., 133.  
 Stirling, W., & Sons, 134.  
 Strecker, 53.  
  
 Tabourin, 241.  
 Tedder, A. V., 419.  
 Templeton, J., & Co., 133.  
 Thénard, P., 147.  
 Thomas, E., 254.  
 Thompson, W. P., 198.  
 Thorp, W., 145.



- |  |   |
|--|---|
| <p> Thorpe, J., 421.<br/> Tiemann, 120.<br/> Tilden, W. A., 315, 347, 348.<br/> Turkey-Red Dyers' Association, 305,<br/> 312.<br/> Turner, J., 419.<br/> Tyndall, 284.<br/> Tyrer, T., &amp; Co., 219.<br/> Tyrer, C., 219.<br/> Tyrer, T., 309, 419.<br/> <br/> Unverdorben, 4, 5, 70, 77, 97, 142, 186.<br/> <br/> Van Dorp, 211.<br/> Van 't Hoff, 315.<br/> Verguin, 17, 81, 156, 159, 242, 243, 300,<br/> 316.<br/> Verneuil, 381.<br/> Vidal, R., 194, 272.<br/> Vignon &amp; Co., 272. </p> | <p> Walker, W., &amp; Son, 132.<br/> Wanklyn, 86.<br/> Watts, 284.<br/> Weldon, 214.<br/> Williams, C. G., 28, 101, 166, 242, 244,<br/> 254, 301.<br/> Williams, Thomas &amp; Dower, 245,<br/> 301.<br/> Wilton, T., 219.<br/> Winckler, C., 190, 213, 250, 255,<br/> 256.<br/> Witt, 145.<br/> Witt, O. N., 67, 69, 80, 99, 115, 118, 122,<br/> 123, 195, 264, 301, 324.<br/> Wöhler, 411.<br/> Worstell, 219.<br/> Würtz, 51, 178.<br/> Wynne, 192.<br/> <br/> Zinin, 4, 9, 65, 77, 142, 187, 238. </p> |
|--|---|

## INDEX OF COLOURING MATTERS

- Acid green, 116, 192.  
     magenta, 192, 228.  
     violet, 192.  
     yellow, 116, 122, 265.  
 Acridine orange, 194.  
     yellow, 194.  
 Aldehyde green, 29, 84, 171, 260.  
 Alizarin, 46, 54, 57, 91, 112, 113, 114,  
     116, 122, 134, 136, 177, 178, 181,  
     183, 194, 199, 228, 229, 245, 246,  
     247, 248, 252, 260, 271, 290, 291,  
     302, 305, 369, 412.  
     blue, 94, 101, 265, 290.  
     Bordeaux, 194.  
     cyanine, 194.  
     orange, 94, 290.  
     saphirole, 194.  
     viridine, 194.  
 Alkali blue, 83, 116.  
 Alkaline green, 63.  
 Aniline black, 40, 194, 254, 291,  
     302.  
     blue, 22, 43, 82, 88, 159, 161, 162, 163,  
     164, 192, 228, 229.  
     pink (see Safranin).  
     purple (see Mauve).  
     red (see Magenta).  
     yellow, 122, 124, 192, 228, 253, 260.  
 Anthracene blue, 194.  
 Anthrapurpurin, 92, 116, 181, 183.  
 Auramine, 116, 192, 228, 230.  
 Aurine, 34, 86, 113, 114, 116.  
 Azodiphenyl blue, 122.  
 Azuline, 35, 83.  
  
 Benzaldehyde green, 84, 88, 90.  
 Benzoflavine, 194.  
 Biebrich scarlet, 116, 123, 265.  
 Bismarck brown, 66, 99, 100, 116, 122,  
     124, 192, 228, 253, 260.  
 Blackley blue, 116.  
     red, 391.  
 Bleu de Lyons (see Aniline blue).  
 Bleu de Paris, 24.  
  
 Blue black, 265.  
 Bordeaux, 100, 116, 265, 291.  
 Brilliant green, 85, 88, 116, 228, 230.  
 Britannia violet, 28, 83, 166, 245, 251,  
     252, 260.  
  
 Cachou de Laval, 194, 265.  
 Carminaphtha, 37.  
 Chloramine yellow, 193.  
 Chrysoidine, 67, 99, 100, 115, 116, 122,  
     175, 192, 228, 265.  
 Clayton yellow, 193.  
 Cochineal, 112, 158, 199.  
 Cœrulein, 265.  
 Congo red, 192, 265.  
 Corraline (see Peonine).  
 Crocein scarlet, 116, 123, 192.  
 Crysaniline (see Phosphine).  
 Crystal violet, 228, 230, 262.  
 Cumidine scarlet, 116.  
 Cyanine, 101, 166, 167, 253, 301.  
 Cyanosin, 116.  
  
 Dahlia, 27, 45, 79, 251.  
 Diphenylamine blue, 63, 116.  
     orange, 116.  
  
 Eosin, 95, 116, 122, 175, 369.  
 Erica, 193.  
 Erythrosin, 116.  
 Ethyl violet, 166.  
  
 Fast red, 100, 265.  
     yellow, 100.  
 Field's orange, 32.  
 Flavaniline, 101, 126, 265.  
 Flavopurpurin, 93, 116, 181.  
 Fleur de Garance, 49, 178, 179.  
 Fluorescein, 95.  
 French purple, 154.  
 Fuchsine (see Magenta).

Gallein, 122, 265.  
Gallocyanin, 228.  
Garancine (see Fleur de Garance).

Helianthine (see Orange III.).  
Hofmann's violet, 25, 44, 60, 83, 102,  
165, 173, 192, 228, 229, 230, 231,  
241, 244, 251, 260, 262, 279, 301.

Immedial black, 195.  
blue, 195.  
Imperial violet, 24, 82, 159, 161, 163.  
Indigo (artificial), 199, 204, 205, 216, 217,  
219, 265, 272, 273, 292, 308, 314,  
316, 323, 369, 412.  
(natural), 71, 97, 98, 117, 123, 199, 204,  
216, 217, 219, 309, 323.  
pure, 219.  
salt, 208, 215.  
Indoine blue, 194.  
Indophenol, 115, 117, 123, 265.  
Indophor, 215.  
Induline, 116, 228, 253, 260.  
scarlet, 194.  
Iodine green, 30, 63, 84, 166, 170, 173,  
228, 229, 230, 260.

Janus dyes, 193.

Katigene black, 195.  
brown, 195.  
green, 195.

Lauth's violet, 173, 264.

Madder, 48, 55, 112, 178, 179, 199, 245,  
302, 323.  
Magdala red, 99, 169.  
Magenta, 16, 17, 18, 19, 20, 38, 43, 60,  
81, 102, 113, 114, 116, 122, 124,  
154, 156, 158, 161, 162, 192, 228,  
241, 242, 243, 244, 251, 253, 262,  
263, 270, 300, 301, 316, 369.  
Malachite green, 63, 84, 116, 122, 192,  
205, 228, 230, 231, 262, 367, 412.  
Manchester brown (see Bismarck brown).  
yellow, 36, 100, 116, 124, 228, 253, 260.  
Martius yellow, 99, 169.  
Mauve, 5, 39, 76, 121, 124, 149, 151, 154,  
160, 161, 165, 174, 234, 239, 240,  
241, 242, 251, 254, 265, 270, 298,  
299, 301, 316.

Meister's scarlet, 100.  
Meldola's blue, 194.  
Metanil yellow, 116.  
Methyl green, 63.  
violet, 62, 88, 114, 116, 192, 228, 230,  
231, 244, 260, 262, 369.  
Methylene blue, 101, 116, 122, 194, 228,  
230, 264, 271.  
Murexide, 269.

Naphthalene red, 170.  
Naphthazarin, 169.  
Naphthol orange, 228, 265.  
yellow, 112, 114, 116, 265.  
Neutral violet, 265.  
Nicholson's blue, 24, 39, 83, 163.  
Night blue, 228, 230, 231, 262.  
Nitroalizarin (see Alizarin orange).  
Nitrosophenylene, 33.

Opal blue, 64.  
Orange I., 116.  
Orange II., 116.  
Orange III., 116.  
Orange IV., 116.

Paranitraniline red, 193, 291.  
Peonine, 34, 83.  
Perkin's green, 31, 166, 252.  
violet (see Mauve).  
Phloxin, 96, 116.  
Phosphine, 21, 101, 126, 129, 164, 192,  
194, 228, 253, 260.  
Picric acid, 33, 228, 253, 269.  
Pittacal, 176.  
Ponceau 2 R, 100, 265.  
Prinuline, 193, 278.  
Propiolic acid, 206, 215.  
Prussian blue, 269.  
Purpurin, 49, 92, 183.  
Pyrogene blue, 195.

Quinoline blue (see Cyanine).  
red, 176.

Regina, 163.  
Rhodamine, 194, 264.  
Rhoduline, 194.  
Roccellin, 116.  
Rosaniline (see Magenta).  
Rose Bengal, 116.  
Roseine (see Magenta).  
Rosinduline, 194.

Rosolic acid (see Aurine).  
Runge's blue, 15, 79.

Safranine, 31, 80, 116, 174, 175, 194, 228,  
251, 265.

Safrosin, 116.

Soluble blue, 24, 88, 163.

Sun yellow, 265.

Tartrazine, 265.

Thioflavine, 193.

Tropæoline o, 67, 115, 122.

Tropæoline oo, 67.

Turmerine, 193.

Tyrian purple (see Mauve).

Vermilline scarlet, 113, 114, 116.

Victoria blue, 90, 116, 192, 230, 231,  
262.

green, 84.

Vidal black, 195, 272.

Violet de Paris, 173.

Violine, 301.

Xylidine red, 168.

scarlet 116, 192.

## TABULAR AND STATISTICAL INFORMATION

	PAGE		PAGE
Alizarin, annual production of, in		Coal-tar dyes, list of those produced	
1869-1873 . . . . .	57	by Perkin & Sons . . . . .	251
chronological history of . . . . .	53	British and German, used in	
Alkali trade production, 1852-1861	317	Britain in 1865 . . . . .	133-136
Anthracene dyes, British patents,		in 1900 . . . . .	197
1855-1905 . . . . .	271	statistics relating to . . . . .	383
Azo dyes, British patents, 1855-		value produced in 1878 . . . . .	58
1905 . . . . .	272	Coal-tar products, British imports	
Badische Anilin- und Soda-Fabrik,		and exports in 1909 . . . . .	285
statistics relating to . . . . .	220	German exports of . . . . .	195
Bayer, F. & Co., statistics relating to	224	German colour works, statistics	
Coal, distillation products of . . . . .	2, 47	relating to . . . . .	198
products obtainable from 100 lbs.		Indigo, value of world's produc-	
of . . . . .	13	tion . . . . .	71, 217, 220
Coal-tar, amount distilled for colour-		Indigo dyes, British patents, 1855-	
making in 1890 . . . . .	286	1905 . . . . .	270
weight of various dyes obtain-		Madder, annual imports of . . . . .	55, 56
able from . . . . .	114	Meister, Lucius & Brüning, statis-	
Coal-tar dyes, British imports,		tics relating to . . . . .	369, 370
1886-1900 . . . . .	197	Patents, numbers taken out by	
British patents, 1885-1905 . . . . .	270	British and German firms . . . . .	198
dyeing power of colours obtain-		Perfumes, natural and synthetic . . . . .	384
able from 1 ton of coal . . . . .	114	Rosaniline dyes, British patents,	
German exports of . . . . .	196	1885-1905 . . . . .	271
imports from Germany in 1913 . . . . .	319	Sulphide dyes . . . . .	273
list of (in 1886), arranged accord-		Sulphuric acid and soda, world's	
ing to origin . . . . .	116	production . . . . .	384

PRINTED IN GREAT BRITAIN BY  
NEILL AND CO., LTD.,  
EDINBURGH.

RETURN TO the circulation desk of any  
University of California Library  
or to the

NORTHERN REGIONAL LIBRARY FACILITY  
Bldg. 400, Richmond Field Station  
University of California  
Richmond, CA 94804-4698

---

ALL BOOKS MAY BE RECALLED AFTER 7 DAYS  
2-month loans may be renewed by calling  
(415) 642-6753

1-year loans may be recharged by bringing books  
to NRLF

Renewals and recharges may be made 4 days  
prior to due date

---

DUE AS STAMPED BELOW

---

**OCT 19 1991**

OCT 13 1993

JAN 16 1999  
APR 25 2000

---

---

---

---

---

---

---

---

---





YC 13757

TP953

B75

1915

349277

Gardner

UNIVERSITY OF CALIFORNIA LIBRARY

